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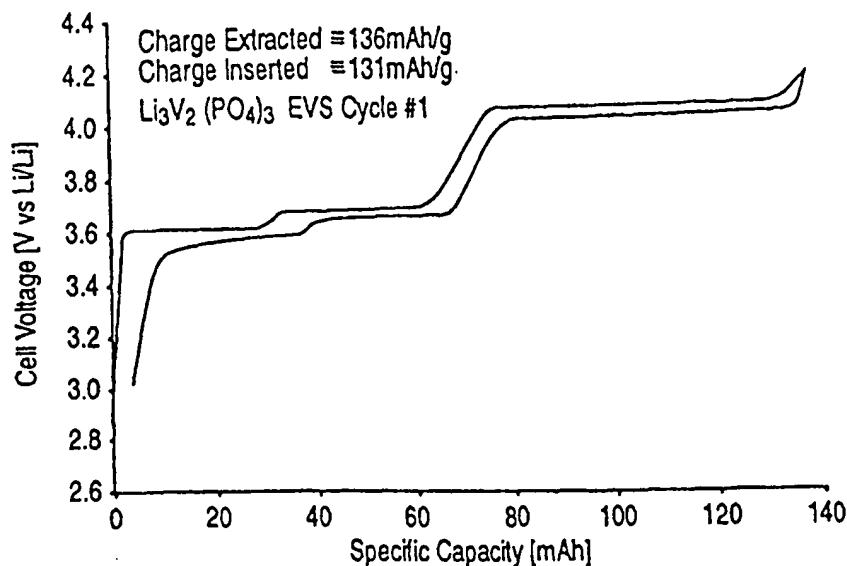
(57) Abstract

The invention provides an electrochemical cell which comprises an electrode having a lithium metal phosphorous compound.

LITHIUM BASED PHOSPHATES FOR USE IN LITHIUM ION BATTERIES AND METHOD OF PREPARATION

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Field of the Invention

This invention relates to improved materials usable as electrode active materials, method for making such improved materials, and electrodes formed from it for electrochemical cells in batteries.

Background of the Invention

Lithium batteries are prepared from one or more lithium electrochemical cells containing electrochemically active (electroactive) materials. Such cells typically include an anode (negative electrode), a cathode (positive electrode), and an electrolyte interposed between spaced apart positive and negative electrodes. Batteries with anodes of metallic lithium and containing metal chalcogenide cathode active material are known. The electrolyte typically comprises a salt of lithium dissolved in one or more solvents, typically nonaqueous (aprotic) organic solvents. Other electrolytes are solid electrolytes typically called polymeric matrixes that contain an ionic conductive medium, typically a metallic powder or salt, in combination with a polymer that itself may be ionically conductive which is electrically insulating. By convention, during discharge of the cell, the negative electrode of the cell is defined as the anode. Cells having a metallic lithium anode and metal chalcogenide cathode are charged in an initial condition. During discharge, lithium ions from the metallic anode pass through the liquid electrolyte to the electrochemical

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active (electroactive) material of the cathode whereupon they release electrical energy to an external circuit.

It has recently been suggested to replace the lithium metal anode with an intercalation anode, such as a
5   lithium metal chalcogenide or lithium metal oxide. Carbon anodes, such as coke and graphite, are also intercalation materials. Such negative electrodes are used with lithium-containing intercalation cathodes, in order to form an electroactive couple in a cell. Such cells, in an initial
10 condition, are not charged. In order to be used to deliver electrochemical energy, such cells must be charged in order to transfer lithium to the anode from the lithium-containing cathode. During discharge the lithium is transferred from the anode back to the cathode. During a
15 subsequent recharge, the lithium is transferred back to the anode where it reintercalates. Upon subsequent charge and discharge, the lithium ions (Li^+) are transported between the electrodes. Such rechargeable batteries, having no free metallic species are called rechargeable ion batteries
20 or rocking chair batteries. See U.S. Patent Numbers 5,418,090; 4,464,447; 4,194,062; and 5,130,211.

Preferred positive electrode active materials include $LiCoO_2$, $LiMn_2O_4$, and $LiNiO_2$. The cobalt compounds are relatively expensive and the nickel compounds are
25 difficult to synthesize. A relatively economical positive electrode is $LiMn_2O_4$, for which methods of synthesis are known, and involve reacting generally stoichiometric quantities of a lithium-containing compound and a manganese containing compound. The lithium cobalt oxide ($LiCoO_2$),
30 the lithium manganese oxide ($LiMn_2O_4$), and the lithium nickel oxide ($LiNiO_2$) all have a common disadvantage in that the charge capacity of a cell comprising such cathodes suffers a significant loss in capacity. That is, the initial capacity available (amp hours/gram) from $LiMn_2O_4$,
35 $LiNiO_2$, and $LiCoO_2$ is less than the theoretical capacity because less than 1 atomic unit of lithium engages in the

electrochemical reaction. Such an initial capacity value is significantly diminished during the first cycle operation and such capacity further diminishes on every successive cycle of operation. The specific capacity for

5    $LiMn_2O_4$ is at best 148 milliamp hours per gram. As described by those skilled in the field, the best that one might hope for is a reversible capacity of the order of 110 to 120 milliamp hours per gram. Obviously, there is a tremendous difference between the theoretical capacity (assuming all

10   lithium is extracted from $LiMn_2O_4$) and the actual capacity when only 0.8 atomic units of lithium are extracted as observed during operation of a cell. For $LiNiO_2$ and $LiCoO_2$ only about 0.5 atomic units of lithium is reversibly cycled during cell operation. Many attempts have been made to

15   reduce capacity fading, for example, as described in U.S. Patent No. 4,828,834 by Nagaura et al. However, the presently known and commonly used, alkali transition metal oxide compounds suffer from relatively low capacity. Therefore, there remains the difficulty of obtaining a

20   lithium- containing chalcogenide electrode material having acceptable capacity without disadvantage of significant capacity loss when used in a cell.

Summary of the Invention

The invention provides novel lithium-containing phosphate materials having a high proportion of lithium per formula unit of the material. Upon electrochemical interaction, such material deintercalates lithium ions, and is capable of reversibly cycling lithium ions. The invention provides a rechargeable lithium battery which comprises an electrode formed from the novel lithium-containing phosphates, preferably lithium-metal-phosphates. Methods for making the novel phosphates and methods for using such phosphates in electrochemical cells are also provided. Accordingly, the invention provides a rechargeable lithium battery which comprises an electrolyte; a first electrode having a compatible active material; and a second electrode comprising the novel phosphate materials. The novel materials, preferably used as a positive electrode active material, reversibly cycle lithium ions with the compatible negative electrode active material. Desirably, the phosphate has a proportion in excess of 2 atomic units of lithium per formula unit of the phosphate, and upon electrochemical interaction the proportion of lithium ions per formula unit become less. Desirably, the lithium-containing phosphate is represented by the nominal general formula $Li_aE'_bE''_c(PO_4)_3$ where in an initial condition "a" is about 3, and during cycling varies as $0 \leq a \leq 3$; b and c are both greater than 0, and b plus c is about 2. In one embodiment, elements E' and E'' are the same. In another embodiment, E' and E'' are different from one another. At least one of E' and E'' is an element capable of an oxidation state higher than that initially present in the lithium phosphate compound. Correspondingly, at least one of E' and E'' has more than one oxidation state. Both E' and E'' may have more than one oxidation state and both may be oxidizable from the state initially present in the phosphate compound. Desirably, at least one

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of E' and E" is a metal or semi-metal. Preferably, at least one of E' and E" is a metal. Preferably, the phosphate is represented by the nominal general formula $Li_3M'_bM''_c(PO_4)_3$, where M' and M" are each metalloids or metals, b plus c is about 2, and M' and M" satisfy the conditions of oxidizability and oxidation state given for E' and E". Many combinations satisfying the above conditions are possible. For example, in one embodiment M' and M" are each transition metals. In still another embodiment of the formulation $Li_3M'_yM''_{2-y}(PO_4)_3$, M' may be selected from non-transition metals and semi-metals (metalloids). In another embodiment, such non-transition metal has only one oxidation state and is nonoxidizable from its oxidation state in the final compound $Li_3M'_yM''_{2-y}(PO_4)_3$. In this case, M' may be selected from metals, such as aluminum, magnesium, calcium, potassium, and other Groups I and II metals. In this case, M" has more than one oxidation state, and is oxidizable from its oxidation state in the end product, and M" is preferably a transition metal. In another embodiment, the non-transition-metal element has more than one oxidation state. In one preferred embodiment, M" is a transition metal, and M' is a non-transition-metal metal. Here, M' may be Mg, Be, Ca, Sn, Pb, Ge, B, K, Al, Ga, In, As or Sb; and M" may be Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Mo, W, Zn, Cd or Pd. For example, M' is +3 and M" is +3 oxidation state. These oxidation states are merely exemplary, as many combinations are possible. In still another preferred embodiment, one metal is Zr or Ti, and the other metal is a metal characterized by a +2 oxidation state. Here, M^{+2} may be Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Sn, Pb, Mo, W, Zn, Cd or Pd. The Zr and Ti each have +4 oxidation state.

Examples of semi-metals having more than one oxidation state are selenium and tellurium; other non-transition metals with more than one oxidation state are tin and lead. Metallic elements include metals and semi-

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metals, such as semi-conductors, including silicon (Si), tellurium (Te), selenium (Se), antimony (Sb), and arsenic (As).

Among the metals and metalloids useful as M', M" or both, there are B (Boron), Ge (Germanium), As (Arsenic), Sb (Antimony), Si (Silicon), and Te (Tellurium). The selenium and sulfur elements are also able to form positive ions but are less desirable. Among the useful metals which are not transition metals, there are the Group IA (New IUPAC 1) alkali; the Group IIA (New IUPAC 2) alkaline; the Group IIIA (13); the Group IVA (14); and the Group VA (15). The useful metals which are transition metals are Groups IIIB (3) to IIB (12), inclusive. Particularly useful are the first transition series transition metals of the 4th Period of the Periodic Table. The other useful transition metals are found in the 5th and 6th Periods, and a few in the 7th Period. Among the useful metals which are not transition metals, there are the Group IA (New IUPAC 1) alkali, particularly Li (Lithium), Na (Sodium), K (Potassium), Rb (Rubidium), Cs (Caesium); the Group IIA (New IUPAC 2) alkaline, particularly Be (Beryllium), Mg (Magnesium), Ca (Calcium), Sr (Strontium), Ba (Barium); the Group IIIA (13) Al (Aluminum), Ga (Gallium), In (Indium), Tl (Thallium); the Group IVA (14) Sn (Tin), Pb (Lead); and the Group VA (15) Bi (Bismuth). The useful metals which are transition metals are Groups IIIB (3) to IIB (12), inclusive. Particularly useful are the first transition series (4th Period of the Periodic Table), Sc (Scandium), Ti (Titanium), V (Vanadium), Cr (Chromium), Mn (Manganese), Fe (Iron), Co (Cobalt), Ni (Nickel), Cu (Copper), Zn (Zinc). The other useful transition metals are Y (Yttrium), Zr (Zirconium), Nb (Niobium), Mo (Molybdenum), Ru (Ruthenium), Rh (Rhodium), Pd (Palladium), Ag (Silver), Cd (Cadmium), Hf (Hafnium), Ta (Tantalum), W (Tungsten), Re (Rhenium), Os (Osmium), Ir (Iridium), Pt (Platinum), Au (Gold), Hg

(Mercury); and the lanthanides, particularly La (Lanthanum), Ce (Cerium), Pr (Praseodymium), Nd (Neodymium), Sm (Samarium). M is most desirably a first transition series transition metal, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn; other desirable transition metals are Zr, Mo, and W. Mixtures of transition metals are also desirable.

The phosphates are alternatively represented by the nominal general formula $Li_{3-x}M'_yM''_{2-y}(PO_4)_3$ ($0 \leq x \leq 3$), signifying capability to deintercalate and reinsert lithium. $Li_{3-x}M'_yM''_{2-y}(PO_4)_3$ signifies that the relative amount of M' and M'' may vary, with $0 \leq y \leq 2$, preferably, some M' and M'' are each present. The same criteria as to the values of x and y apply to $Li_{3-x}E'_yE''_{2-y}(PO_4)_3$. The active material of the counter electrode is any material compatible with the lithium-metal-phosphate of the invention. Where the lithium-metal-phosphate is used as a positive electrode active material, metallic lithium may be used as the negative electrode active material where lithium is removed and added to the metallic negative electrode during use of the cell. The negative electrode is desirably a nonmetallic intercalation compound. Desirably, the negative electrode comprises an active material from the group consisting of metal oxide, particularly transition metal oxide, metal chalcogenide, carbon, graphite, and mixtures thereof. It is preferred that the anode active material comprises graphite. The lithium-metal-phosphate of the invention may also be used as a negative electrode material.

The present invention resolves the capacity problem posed by widely used cathode active material. It has been found that the capacity of cells having the preferred $Li_3M'M''(PO_4)_3$ active material of the invention are greatly improved, for example, over $LiMn_2O_4$. Optimized cells containing lithium-metal-phosphates of the invention potentially have performance greatly improved over all of

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the presently used lithium metal oxide compounds.
Advantageously, the novel lithium-metal-phosphate compounds
of the invention are relatively easy to make, and readily
adaptable to commercial production, are relatively low in
5   cost, and have very good specific capacity.

Objects, features, and advantages of the
invention include an improved electrochemical cell or
battery based on lithium which has improved charging and
discharging characteristics, a large discharge capacity,
10 and which maintains its integrity during cycling. Another
object is to provide a cathode active material which
combines the advantages of large discharge capacity and
with relatively lesser capacity fading. It is also an
object of the present invention to provide positive
15 electrodes which can be manufactured more economically and
relatively more conveniently, rapidly, and safely than
present positive electrodes which react readily with air
and moisture. Another object is to provide a method for
forming cathode active material which lends itself to
20 commercial scale production providing for ease of preparing
large quantities.

These and other objects, features, and advantages
will become apparent from the following description of the
preferred embodiments, claims, and accompanying drawings.

25

Brief Description of the Drawings

Figure 1 is an EVS (Electrochemical Voltage Spectroscopy) voltage/capacity profile for a cell embodying the lithium-metal-phosphate material of the invention $Li_3V_2(PO_4)_3$ in combination with a lithium metal counter electrode in an electrolyte comprising ethylene carbonate (EC) and dimethyl carbonate (DMC) in a weight ratio of 2:1 and including a 1 molar concentration of $LiPF_6$ salt. The lithium-metal-phosphate containing electrode and the lithium metal counter electrode are maintained spaced apart by a separator of fiber glass which is interpenetrated by the solvent and the salt. The conditions are ± 10 mV steps, between about 3.0 and 4.2 volts, and the critical limiting current density is less than or equal to 0.05 mA/cm^2.

Figure 2 is an EVS differential capacity plot for the cell as described in connection with **Figure 1**.

Figure 3 is a voltage/capacity plot of $Li_3V_2(PO_4)_3$ cycled with a lithium metal anode using constant current cycling at ± 0.2 milliamps per square centimeter in a range of 3.0 to 4.3 volts.

Figure 4 is a two-part graph based on multiple constant current cycling of $Li_3V_2(PO_4)_3$ cycled with a lithium metal anode using the electrolyte as described in connection with **Figure 1** and cycled, charge and discharge at ± 0.25 milliamps per square centimeter, 3.0 to 4.2 volts. In the two-part graph, **Figure 4A** shows the excellent rechargability of the lithium-metal-phosphate/lithium metal cell. **Figure 4B** shows the excellent cycling and capacity of the cell.

Figure 5 is an illustration of a cross section of a thin battery or cell embodying the invention.

Figure 6 shows the results of an x-ray diffraction analysis of the $Li_3V_2(PO_4)_3$ prepared according to the invention using CuKα radiation, λ = 1.5418 Å.

Figure 7 is an EVS voltage/capacity profile for
5   a cell containing $Li_3AlV(PO_4)_3$ positive electrode of the invention in combination with a lithium metal counter-electrode in an electrolyte as described with respect to Figure 1 above. The conditions of the test are as described with respect to Figure 1 above.

Figure 8 is an EVS differential capacity plot for
10   the cell as described in connection with Figure 7.

Figure 9 shows the results of the first constant current cycling at plus/minus 0.05 milliamps per square centimeter between about 3 and 4.5 volts based on the
15   $Li_{3-x}AlV(PO_4)_3$ active material in the cathode.

Figure 10 is a graph based on multiple constant current cycling at plus/minus 0.05 milliamps per square centimeter versus metallic lithium counter-electrode.

Figure 11 is a voltage/capacity plot of
20   $Li_3V_2(PO_4)_3$ cycled with a carbon-based negative electrode using constant current cycling at plus/minus 0.2 milliamps per square centimeter in a range of 2.5 to 4.1 volts.

Figure 12 presents data obtained by multiple current cycling at about plus/minus 0.2 milliamps per
25   square centimeter between about 2.5 to 4.1 volts.

Figure 13 is an EVS voltage/capacity profile for a cell containing $Li_3AlV(PO_4)_3$ positive electrode made under H_2 atmosphere cycled with a lithium metal counter-electrode in an electrolyte. The cell is as described with respect
30   to Figure 1 above. The conditions of the test are also as described with respect to Figure 1 above.

Figure 14 is an EVS differential capacity plot for the cell as described in connection with Figure 13.

Figure 15 shows the results of the first constant
35   current cycling at plus/minus 0.05 milliamps per square centimeter between about 3 and 4.2 volts based on the

$Li_{3-x}AlV(PO_4)_3$ active material in the cathode prepared under H_2 atmosphere.

<u>Detailed Description of the</u>
<u>Preferred Embodiments</u>

The present invention provides lithium-containing
5   phosphate materials, preferably lithium-metal-phosphates,
which are usable as electrode active materials, for
the first time, as a source of lithium (Li^+) ions.
Upon extraction of x lithium ions from the preferred
$Li_{3-x}M'M''(PO_4)_3$, significant capacity is achieved. Such
10   specific capacity achieved from preferred lithium-metal-
phosphates is far in excess of the specific capacity from
$Li_xMn_2O_4$ ($Li_{1-x}Mn_2O_4$), an example of a currently used cathode
active material. In the method of the invention,
electrochemical energy is provided by deintercalation of
15   lithium from lithium-metal-phosphates ($Li_3M'M''(PO_4)_3$). For
example, when lithium is removed per formula unit of the
$Li_3M'M''(PO_4)_3$, vanadium is oxidized from vanadium III to
vanadium IV or V in $Li_3M_2(PO_4)_3$, $M_2 = V_2$.

When 1 lithium is removed per formula unit of the
20   lithium vanadium phosphate, V^{III} is oxidized to V^{IV}. The
electrochemical reaction is as shown below:

$$Li_3V^{+3}V^{+3}(PO_4)_3 \rightarrow Li_2V^{+3}V^{+4}(PO_4)_3 + Li^+ + e^-$$
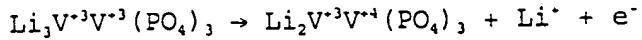
25   Further extraction is possible according to:

$$Li_2V^{+3}V^{+4}(PO_4)_3 \rightarrow Li_1V^{+4}V^{+4}(PO_4)_3 + Li^+ + e^-$$
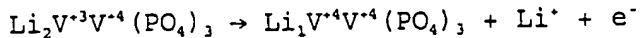
Note that the average oxidation state of vanadium is +4
30   (IV). It is thought that both of the vanadium atomic
species carry a +4 charge, it is less likely that one of
the vanadium species carries a +3 charge and the other a +5
charge. Advantageously, still further oxidation is
possible with the removal of the final lithium ion
35   according to the Equation:

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$$Li_1V^{+4}V^{+4}(PO_4)_3 \rightarrow V^{+4}V^{+5}(PO_4)_3 + Li^+ + e^-$$
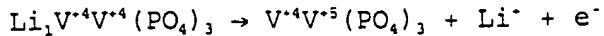
In the overall equation $Li_3V^{+3}V^{+3}(PO_4)_3 \rightarrow V^{+4}V^{+5}(PO_4)_3 + 3Li^+ + 3e^-$, this material has a theoretical capacity of 197 milliamp hours per gram upon electrochemical oxidation as per the reaction shown herein. The electrochemical extraction of lithium from $Li_3M'M''(PO_4)_3$ is heretofore not known to have been described. Similarly, a mixed metal compound, such as $Li_3FeV(PO_4)_3$, has two oxidizable elements. In contrast, $Li_3AlTm(PO_4)_3$ has one oxidizable metal, the transition metal (Tm).

Figures 1 through 4 which will be described more particularly below shows capacity in actual use where the lithium-metal-phosphate cathode (positive electrode) of the invention was tested in a cell comprising a lithium metal counter electrode (negative electrode) and an $EC:DMC-LiPF_6$ electrolyte, with operation between about 3.0 and 5.0 volts versus L/Li^+ where lithium is cycled between the positive electrode and the negative electrode.

In another aspect, the invention provides a lithium ion battery which comprises an electrolyte; a negative electrode having an intercalation active material; and a positive electrode comprising a lithium-metal-phosphate active material characterized by an ability to deintercalate lithium ions for intercalation into the negative electrode active material. The lithium-metal-phosphate is desirably represented by the nominal general formula $Li_3M'M''(PO_4)_3$. In one aspect, the metals M' and M" are the same and in another aspect, the metals M' and M" are different. Desirably, the phosphate is the compound $Li_3M_2(PO_4)_3$ where M is a transition metal, and M is most desirably V, Fe, Cr, Ni, Co, and Mn. The lithium-metal-phosphate is preferably a compound represented by the nominal general formula $Li_{3-x}V_2(PO_4)_3$, signifying the preferred composition and its capability to deintercalate lithium. The present invention resolves a capacity problem

posed by conventional cathode active materials. Such problems with conventional active materials are described by Tarascon in U.S. Patent No. 5,425,932, using $LiMn_2O_4$ as an example. Similar problems are observed with $LiCoO_2$,

5   $LiNiO_2$, and many, if not all, lithium metal chalcogenide materials. The present invention demonstrates that such capacity problems are overcome and greater proportion of available capacity in the cathode active material is utilizable providing a great improvement over conventional

10 active materials.

The positive electrode active material in an initial condition is represented by the molecular formula $Li_{3-x}M'M''(PO_4)_3$. When used in a cell it deintercalates a quantity of x lithium ions for intercalation into the

15 negative electrode, where the amount of x ions deintercalated is greater than 0 and less than or equal to 3. Accordingly, during cycling, charge and discharge, the value of x varies as x greater than or equal to 0 and less than or equal to 3.

20 Positive electrode lithium-metal-phosphate active material was prepared and tested in electrochemical cells and the results are reported in **Figures 1** through **4**. A typical cell configuration will be described with reference to **Figure 5**.

25 A description of the electrochemical cell or battery which uses the novel active material of the invention will now be described. By convention, an electrochemical cell comprises a first electrode, a counter electrode which reacts electrochemically with the first

30 electrode, and an electrolyte which is capable of transferring ions between the electrodes. A battery refers to one or more electrochemical cells. Referring to **Figure 5**, an electrochemical cell or battery 10 has a negative electrode side 12, a positive electrode side 14, and an

35 electrolyte/separator 16 therebetween. The negative electrode is the anode during discharge, and the positive

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electrode is the cathode during discharge. The negative
electrode side includes current collector 18, typically of
nickel, iron, stainless steel, and copper foil, and
negative electrode active material 20. The positive
5   electrode side includes current collector 22, typically of
aluminum, nickel, and stainless steel, and such foils may
have a protective conducting coating foil, and a positive
electrode active material 24. The electrolyte/separator 16
is typically a solid electrolyte, or separator and liquid
10   electrolyte. Solid electrolytes typically referred to as
polymeric matrixes which contain an ionic conductive
medium. Liquid electrolytes typically comprise a solvent
and an alkali metal salt which form an ionically conducting
liquid. In this latter case, the separation between the
15   anode and cathode is maintained, for example, by a
relatively inert layer of material such as glass fiber. The
electrolyte is not an essential feature of the invention.
Essentially, any lithium ion containing conducting
electrolyte may be used, that is stable up to 4.5 volts or
20   more. Essentially any method may be used to maintain the
positive and negative electrodes spaced apart and
electrically insulated from one another in the cell.
Accordingly, the essential features of the cell are the
positive electrode, a negative electrode electrically
25   insulated from the positive electrode, and an ionically
conducting medium between the positive and negative
electrodes. Examples of a suitable separator/electrolyte,
solvents, and salts are described in U.S. Patent No.
4,830,939 showing a solid matrix containing an ionically
30   conducting liquid with an alkali metal salt where the
liquid is an aprotic polar solvent; and U.S. Patent Numbers
4,935,317; 4,990,413; 4,792,504; and 5,037,712. Each of the
above patents is incorporated herein by reference in its
entirety.
35   Electrodes of the invention are made by mixing a
binder, the active material, and carbon powder (particles

15

of carbon). The binder desirably is a polymer. A paste
containing the binder, active material, and carbon, is
coated onto a current collector.

5   Positive Electrode

A positive electrode containing the lithium
phosphate compound, preferably lithium-metal-phosphate,
active material of the invention is prepared by the
following method. For the positive electrode, the content
10 was as follows: 50 to 90 percent by weight active material
($Li_3M'M''(PO_4)_3$); 5 to 30 percent carbon black as the
electrically conductive diluent; and 3 to 20 percent
binder. The stated ranges are not critical. The amount of
active material may range from 25 to 85 weight percent. The
15 formation of each electrode will now be described. The
positive electrode was prepared from mixtures of lithium-
metal-phosphate (active material) and EPDM (ethylene
propylene diene monomer) as the binder, Shawinigan Black®
was used as the carbon powder conductive diluent. The
20 carbon powder conductive diluent is used to enhance
electronic conductivity of the lithium-metal-phosphate.
Shawinigan Black®, available from Chevron Chemical Company,
San Ramone, California, has a BET average surface area of
about 70 ± 5 square meters per gram. Other suitable carbon
25 blacks are sold under the designation Super P™ and Super S™
available from MMM, a subsidiary of Sedema, which carbons
have BET surface areas of about 65 ± 5 square meters per
gram. (MMM has its headquarters in Brussels, Belgium.)
Examples of suitable polymeric binders include EPDM
30 (ethylene   propylene   diene   termonomers),   PVDF
(polyvinylidene difluoride), ethylene acrylic acid
copolymer, EVA (ethylene vinyl acetate copolymer),
copolymer mixtures, and the like. It is desirable to use
either PVDF available from Polysciences Corporation with a
35 molecular weight of 120,000 or EPDM available from Exxon
Corporation and sold under the designation EPDM 2504™. EPDM

is also available from The Aldrich Chemical Company. The
description of carbon powders and binders constitute
representative examples and the invention is not limited
thereby. For example, other carbon powders are available
5   from Exxon Chemicals, Inc., Chicago, Illinois under the
trade name Ketjen Black EC 600 JD® and polyacrylic acid of
average molecular weight 240,000 is commercially available
from BF Goodrich, Cleveland, Ohio under the name Good-Rite
K702™. The positive electrodes of the invention comprised
10   mixtures of the lithium-metal-phosphate active material,
the binder (EPDM), and the carbon particles (Shawinigan
Black®). These were mixed and blended together with a
solvent. Xylene is a suitable solvent. The mixture was
then coated onto an aluminum foil current collector to
15   achieve a desired thickness for the final electrode.

Electrolyte

The electrolyte used to form the completed cell
is preferably a combination of EC/DMC when a carbon counter
20   electrode is used. That is, ethylene carbonate (EC) and
dimethyl carbonate (DMC). The ratio of EC:DMC was about
2:1 by weight. Generally, when a lithium metal anode is
used, the choice of an electrolyte is less restricted. It
may be the EC:DMC in a ratio of 2:1 by weight or, for
25   example, EC:PC (propylene carbonate) in 50:50 by weight
ratio. In any case, the preferred salt is 1 molar $LiPF_6$.
Positive and negative electrodes are maintained in a
separated condition using a fiber glass layer. Such
separation can also be achieved using a layer of Celgard™.
30   Hoechst - Celanese Corp., Celgard 2400™, porous
polypropylene, 25 microns thick.

Negative Electrode

The electrochemical cell used with the positive
35   electrode and electrolyte may contain one of a variety of
negative electrode active materials. In one embodiment,

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the negative electrode may be metallic lithium. In more desirable embodiments, the negative electrode is an intercalation active material, such as, metal oxides and graphite. When a metal oxide active material is used, the

5   components of the electrode are the metal oxide, electrically conductive carbon black, and binder in the proportions as described above for the positive electrode. Representative, but not limiting, examples include coke, graphite, WO_3, Nb_2O_5, and V_6O_{13}. In a preferred embodiment,

10 the negative electrode active material is graphite particles. For test purposes, for determining capacity of a positive electrode, test cells were fabricated using the lithium metal active material. When test cells are formed such as to be used as batteries, a nonmetallic

15 intercalation graphite electrode is preferred. The preferred graphite-based negative electrode comprises about 80 to 95 percent by weight graphite particles, and more preferably about 90 percent by weight with the balance constituted by a binder. Preferably, the anode is prepared

20 from a graphite slurry as follows. A polyvinylidene difluoride (PVDF) solution is prepared by mixing 300 grams of 120,000 MW PVDF (PolyScience) in 300 ml of dimethyl formamide. The mixture was stirred for 2 to 3 hours with a magnetic stirrer to dissolve all of the PVDF. The PVDF

25 functions as a binder for the graphite in the anode. Next, a PVDF/graphite slurry is prepared by first adding 36 grams of graphite (SFG-15) into about 38.5 grams of the PVDF solution. The mixture is homogenized with a commercial homogenizer or blender. (For example, Tissue Homogenizer

30 System from Cole-Parmer Instrument Co., Niles, IL). The viscosity of the slurry is adjusted to about 200 cp with additional PVDF solution. The slurry is coated onto a bare copper foil by standard solvent casting techniques, such as by a doctor blade type coating. (Alternatively, the slurry

35 can be coated onto a copper foil having a polymeric adhesion promoter layer, described above.) In preparing the

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slurry, it is not necessary to grind or dry the graphite, nor is it necessary to add conductive carbon black to the graphite anode formulation. Finally, the electrodes are dried at approximately 150°C for 10 hours to remove

5   residual water prior to making the electrochemical cells.

In one embodiment, the negative electrode has the lithium-metal-phosphate compound as the active material. In the case of $Li_3V^{+3}V^{+3}(PO_4)_3$, the V^{+3} would theoretically be reduced to V^{+2}. For $Li_3Fe^{+3}Fe^{+3}(PO_4)_3$, the same activity is

10   theoretically possible, since Fe^{+2} is a stable and common oxidation state for Fe. This should allow two more lithium ions to be inserted. That is, $Li_{3-x}Fe_2(PO_4)_3$, x is about 2.

Various methods for fabricating electrochemical cells and for forming electrode components are described

15   herein.   The invention is not, however, limited by any particular fabrication method as the novelty lies in the unique positive electrode material itself and combination of positive and negative electrode materials.   Examples of forming cells containing a variety of electrodes and

20   electrolytes can be found in U.S. Patent Nos. 4,668,595; 4,830,939; 4,935,317; 4,990,413; 4,792,504; 5,037,712; 5,262,253; 5,300,373; 5,435,054; 5,463,179; 5,399,447; 5,482,795 and 5,411,820; each of which is incorporated herein by reference in its entirety.   Note that the older

25   generation of cells contained organic polymeric and inorganic electrolyte matrix materials, with the polymeric being most preferred.   The polyethylene oxide of 5,411,820 is an example.   More modern examples are the VDF:HFP polymeric matrix.   Examples of casting, lamination and

30   formation of cells using VdF:HFP are as described in U.S. Patent Nos. 5,418,091; 5,460,904; 5,456,000; and 5,540,741; assigned to Bell Communications Research, each of which is incorporated herein by reference in its entirety.

The compositions of the invention are prepared by

35   mixing together appropriate proportions of precursor compounds.   In one preferred embodiment, precursor

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compounds are in powder form, mixtures of such powders are intermingled and then heated at a temperature sufficient to cause formation of the desired lithium-phosphates of the invention. In this example, the compositions of the

5   invention are prepared by mixing together appropriate proportions of: alkali metal carbonate, here lithium metal carbonate (Li_2CO_3); a phosphoric acid derivative, preferably the phosphoric acid ammonium acid salt, ammonium phosphate, $NH_4H_2(PO_4)$ or $(NH_4)_2H(PO_4)$; and selected metal salts and

10   metal oxides, preferably, MO_x, $0 < x \leq 3$; phosphates, nitrates and acetates. Examples are, MgO, $Mg_3(PO_4)_2$, $Mg(NO_3)_2$, MnO, MnO_2, Mn_2O_3, MoO_2, MoO_3, FeO, Fe_2O_3, Cr_2O_3, ZrO_2, NiO, CoO, VO, V_2O_3, V_2O_5, CuO, TiO, TiO_2, $LiAlO_2$, AlOH, Al_2O_3, $AlPO_4$, B_2O_3, BPO_4, K_2O, SnO, SnO_2, PbO, PbO_2, $Ga(NO_3)_3$, Ga_2O_3,

15   In_2O_3, $In(NO_3)_3$, As_2O_3, Sb_2O_3, BeO, CaO, $Ca_3(PO_4)_2$, $Ca(NO_3)_2$, GeO_2, zinc acetate, ZnO, $Zn(NO_3)_2$, CdO and $Cd(NO_3)_2$. The selection of precursor in part depends on whether a reducing, inert or ambient atmosphere is used.

     In one embodiment, in order to obtain

20   compositions of the compound $Li_3V_2(PO_4)_3$, appropriate mixtures of Li_2CO_3; V_2O_5 or V_2O_3; and $NH_4H_2PO_4$ are used. The proportions are on the basis of molar ratios. The mixture is heated for a number of hours, and at a temperature sufficient to decompose the phosphate. Then the mixture is

25   held at an elevated temperature of about 700°C to about 950°C for several hours. Repeated cooling, grinding and reheating at an elevated temperature may be necessary in order to cause complete reaction to form the final product.

     In another embodiment, a product of the nominal

30   general formula $Li_3AlV(PO_4)_3$, is prepared by mixing appropriate amounts of Li_2CO_3; $Al(OH)_3$ or Al_2O_3; V_2O_5 or V_2O_3; and $NH_4H_2PO_4$. The relative molar proportions are selected based on the atomic amounts of each component in the final product. Those skilled in the art will also recognize that

35   preparation by the sol-gel is advantageous, facilitating cycling since the compound is not as crystal-like.

Amorphous materials often provide plateaus on cycling that are less defined. NASICON phases are commonly known in rhombehedral or monoclinic structure. Some exist in more than one form. The form of the product depends on the

5   method of preparation. Therefore, the degree of crystallinity changes, depending on particle size and process parameters.

The Examples below show methods of preparing compounds of the nominal general formula $Li_3M'M''(PO_4)_3$. The

10 method comprises providing a lithium-containing compound, one or more metal oxide compounds, and a phosphoric acid containing compound. Preferably, the lithium-containing compound is a lithium salt and the phosphoric acid compound is a phosphoric acid salt. The lithium compound, one or

15 more metal or metalloid compounds, and phosphoric acid based compound are mixed together in a proportion which provides the stated nominal general formula. Such precursor compounds are intimately mixed and then reacted together where the reaction is initiated by heat and is

20 desirably conducted in a nonoxidizing, preferably reducing atmosphere, whereby the lithium, M from the metal/metalloid compound (oxide) and phosphate combine to form the $Li_3M'M''(PO_4)_3$. The temperatures required to decompose precursor(s), initiate reaction and then complete the

25 reaction depend, in part, on the precursors. A first heating is at a first temperature of about 550°C to about 750°C, and a second heating is at a second temperature of about 800°C to about 1000°C. Before reacting the compounds, the particles are intermingled to form an

30 essentially homogeneous powder mixture of the precursors. Such intermingling is preferably conducted by forming a wet mixture using a volatile solvent and then the intermingled particles are pressed together in pellet form in grain-to-grain contact with one another. Although it is desired

35 that the precursor compounds be present in a proportion which provides the stated general formula of the product,

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the lithium compound may be present in an excess amount on
the order of 5 percent excess lithium compared to a
stoichiometric mixture of the precursors. Although a number
of lithium compounds are available as precursors, such as
5   lithium acetate, lithium hydroxide, and lithium nitrate,
lithium carbonate (Li_2CO_3) is preferred for the solid state
reaction. The aforesaid precursor compounds are generally
crystals, granules, and powders and are generally referred
to as being in particle form. Although many types of
10   phosphate salts are known, it is preferred to use ammonium
phosphate ($(NH_4)_2HPO_4$). In the case where the compound of the
formulation $Li_3M'M''(PO_4)_3$ is desired where M and M' are the
same metal, a transition metal, such as vanadium, a
suitable precursor is vanadium pentoxide (V_2O_5).

15   The starting materials are available from a
number of sources. The following are typical. Vanadium
pentoxide of the general formula V_2O_5 is obtainable from any
number of suppliers including Kerr McGee, Johnson Matthey,
or Alpha Products of Davers, Massachusetts. It had a
20   melting point of about 690°C, decomposed at 1750°C, a
particle size of less than about 60 mesh (250 microns) and
had a specific gravity of 3.357 grams per cc at 18°C. It
was a yellow-red crystalline powder. Vanadium pentoxide
has a CAS number of 1314-62-1. Alternatively, the vanadium
25   pentoxide may be prepared from ammonium metavanadate
(NH_4VO_3). The ammonium metavanadate is heated to a
temperature of about 400°C to about 450°C to decompose it
to vanadium pentoxide (V_2O_5). Processes for production
of vanadium pentoxide are described in U.S. Patent Numbers
30   3,728,442, 4,061,711 and 4,119,707, each of which is
incorporated herein by reference in its entirety.

         In another embodiment, for the formation of
$Li_3M'M''(PO_4)_3$, where M' and M'' are different from one
another and are metals, preferably transition metals, one
35   may select two different metal oxide powders, such as
titanium oxide (TiO_2), vanadium oxide (V_2O_5, V_2O_3), iron

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oxide (FeO, Fe$_2$O$_3$), chromium oxide (CrO$_2$, CrO, Cr$_2$O$_3$), manganese oxide (MnO$_2$, Mn$_3$O$_4$), cobalt oxide (CoO), nickel oxide (NiO), copper oxide (CuO), molybdenum oxide (MoO$_2$, MoO$_3$) and zinc and zirconium compounds, and the like. In

5   still another embodiment where the formulation Li$_3$M'M"(PO$_4$)$_3$ comprises two different metals, M' and M", one metal M' may be selected from non-transition metals and semi-metals. In another embodiment, non-transition metal has only one oxidation state and is nonoxidizable from its oxidation

10   state in the final compound Li$_3$M'M"(PO$_4$)$_3$. In this case, M' may be selected from metals, such as aluminum and magnesium, calcium, potassium, and other Groups I and II metals, alkali Group I, and semi-metals. Semi-metals are located in the Periodic Table on the right hand side and

15   roughly separate the nonmetals from metals, as is well known in the art. In this case, M" is a metal having more than one oxidation state, and is oxidizable from its oxidation state in the end product, and M" is preferably a transition metal. Examples are Li$_3$KCr(PO$_4$)$_3$ and Li$_3$KMo(PO$_4$)$_3$,

20   where the transition metal (Tm) is, respectively, chromium and molybdenum. See also Tables A to G showing exemplary mixed metal combinations, oxidation states on removal of Li, and active material capacity.

25   <u>Example I</u>

A preferred procedure for forming the Li$_3$M'M"(PO$_4$)$_3$ compound active material will now be described. The method for making Li$_3$M'M"(PO$_4$)$_3$ will be illustrated by formation of Li$_3$V$_2$(PO$_4$)$_3$ (Li$_3$M$_2$(PO$_4$)$_3$). The

30   basic procedure comprised conducting a reaction between a lithium compound, preferably lithium carbonate (Li$_2$CO$_3$), a metal oxide, preferably vanadium pentoxide (V$_2$O$_5$), and a phosphoric acid derivative, preferably the phosphoric acid ammonium acid salt, ammonium phosphate, NH$_4$H$_2$(PO$_4$) or

35   (NH$_4$)$_2$H(PO$_4$). Each of the precursor starting materials are available from a number of chemical outfits including

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Aldrich Chemical Company and Fluka. The $Li_3V_2(PO_4)_3$ was prepared with approximately a stoichiometric mixture of Li_2CO_3, V_2O_5, and $(NH_4)_2HPO_4$. However, a 5 percent excess of lithium (as lithium carbonate) was used to minimize any

5   lithium loss as (Li_2O). The precursor materials were initially intimately mixed and ground for about 30 minutes in a methanol solution. The intimately mixed compounds were then dried and pressed into pellets. Reaction was conducted by heating in an oven at a preferred ramped

10   heating rate of 1°C per minute up to a temperature of about 725°C, and held at 725°C for about 12 hours to decompose the carbonate. Then heating continued at the same ramp rate (1°C per minute) up to a temperature of about 875°C. The mixture was held at this temperature for about 24

15   hours. The entire reaction was conducted in a reducing atmosphere under flowing pure hydrogen gas. The flow rate will depend upon the size of the oven and the quantity needed to maintain a reducing atmosphere. Based on the size of the oven used in this example a flow rate of 25

20   cubic centimeters per minute was used. The oven was permitted to cool down at the end of the 24 hour period, where cooling occurred at a rate of about 3°C per minute. Then the entire procedure was repeated once again for a further 24 hours. The repeated steps were also conducted

25   under reducing atmosphere. Although hydrogen gas was selected to provide the reducing atmosphere, other means for obtaining the reducing atmosphere may be used.

         The general aspects of the above synthesis route are applicable to a variety of starting materials. For

30   example, LiOH and $LiNO_3$ salts may replace Li_2CO_3 as the source of lithium. In this case, the temperature for the first step will vary due to the differing melting points, 450°C for LiOH and 700°C for $LiNO_3$. The vanadium oxide V_2O_5 (V^{+5}), combined with the oxidizing power of the phosphate

35   anion, is required to be offset by a strong reducing agent, for example, the hydrogen atmosphere. Alternatively, lower

oxidation state vanadium complexes could be used, e.g., V_2O_3. This is a vanadium in the 3+ state. But because of the presence of PO_4, a certain degree of oxidation might occur. Therefore, a reducing agent is used. For example,

5   a mixture of 90:10 of $Ar:H_2$ can be used. The same considerations apply to other lithium-metal- and phosphate-containing precursors. The relative oxidizing strength of the selected precursors, and the melting point of the salts will cause adjustment in the general procedure, such as,

10   selection of the reducing agent, its reducing capability and flow rate, and the temperature of reaction.

The final product appeared lime-green in color, and its $CuK\alpha$ x-ray diffraction pattern contained all of the peaks expected for this material as shown in **Figure 6**. The

15   x-ray diffraction was conducted using $CuK\alpha$ radiation, $\lambda = 1.5418$ Å. The pattern evident in **Figure 6** is consistent with a single oxide compound $Li_3V_2(PO_4)_3$. This is evidenced by the position of the peaks in terms of the scattering angle 2 θ (theta), x axis. The x-ray pattern showed no

20   peaks due to the presence of precursor oxides indicating that the solid state reaction is essentially entirely completed. Chemical analysis for lithium and vanadium by atomic absorption spectroscopy showed, on a percent by weight basis, 5.17 percent lithium and 26 percent vanadium.

25   This is close to the expected result of 5.11 percent lithium and 25 percent vanadium.

The chemical analysis and x-ray pattern demonstrate that the product of the invention was indeed the nominal general formula $Li_3V_2(PO_4)_3$ corresponding to the

30   more generic nominal general formula $Li_3M'M''(PO_4)_3$. The term "nominal general formula" refers to the fact that the relative proportion of atomic species may vary slightly on the order of 2 percent to 5 percent, or more typically, 1 percent to 3 percent.

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Example II

The $Li_3V_2(PO_4)_3$, prepared as described immediately above, was tested in an electrochemical cell. The positive electrode was prepared as described above under the section designated "Positive Electrode". The negative electrode was metallic lithium. The electrolyte was a 2:1 weight ratio mixture of ethylene carbonate and dimethyl carbonate within which was dissolved 1 molar $LiPF_6$. The cell was cycled between about 3.0 and about 4.3 volts with performance as shown in Figures 1, 2, 3, 4A, and 4B.

Figure 1 shows a voltage profile of the test cell, based on the $Li_3M'M''(PO_4)_3$ positive electrode active material of the invention, and using a lithium metal counter electrode as described in the examples. The data shown in Figure 1 is based on the Electrochemical Voltage Spectroscopy (EVS) technique. Electrochemical and kinetic data were recorded using the Electrochemical Voltage Spectroscopy (EVS) technique. Such technique is known in the art as described by J. Barker in Synth, Met 28, D217 (1989); Synth. Met. 32, 43 (1989); J. Power Sources, 52, 185 (1994); and Electrochemical Acta, Vol. 40, No. 11, at 1603 (1995). Figure 1 clearly shows and highlights the very high and unexpected degree of reversibility of the lithium ion reactions of the $Li_3M'M''(PO_4)_3$, specifically $Li_3V_2(PO_4)_3$, active material of the invention. The positive electrode contained about 16.8 milligrams of the $Li_3V_2(PO_4)_3$ active material. The total electrode weight including the binder and conductive carbon diluent was about 31.2 milligrams. The positive electrode showed a performance of about 136 milliamp hours per gram on the first discharge. In Figure 1, the capacity in is essentially 136 milliamp hours per gram, and the capacity out is essentially 131 milliamp hours per gram, resulting in essentially no capacity change. Figure 2 is an EVS differential capacity plot based on Figure 1. As can be seen from Figure 2, the relatively symmetrical nature of peaks indicates good

electrical reversibility, with none related to irreversible reactions, since all peaks above the axis (cell charge) have corresponding peaks below the axis (cell discharge), and there is essentially no separation between the peaks
5   above and below the axis.

Figure 3 shows the results of the first constant current cycling at 0.20 milliamps per square centimeter between about 3.0 and 4.3 volts based upon about 16.8 milligrams of the $Li_3V_2(PO_4)_3$ active material in the cathode
10   (positive electrode). In an as prepared, as assembled, initial condition, the positive electrode active material is $Li_3V_2(PO_4)_3$. The lithium is deintercalated from the $Li_3V_2(PO_4)_3$ during charging of the cell. When fully charged, about 2 units of lithium have been removed per
15   formula unit of the original lithium-vanadium-phosphate. Consequently, the positive electrode active material corresponds to $Li_{3-x}V_2(PO_4)_3$ where x is greater than 0 and less than 3, and in the operation of this cell, x appears to be equal to about 2, when the cathode material is at 4.2
20   volts versus Li/Li·. In this charged condition, the electrochemical potential versus lithium of the $Li_1V_2(PO_4)_3$ is about 4.2 volts. The deintercalation of 2 lithium from $Li_3V_2(PO_4)_3$ resulting in the $Li_1V_2(PO_4)_3$, represents approximately 127 milliamp hours per gram corresponding to
25   about 2.2 milliamp hours based on 16.8 milligrams active material. Next, the cell is discharged whereupon a quantity of lithium is reintercalated into the $Li_1V_2(PO_4)_3$. The average voltage is approximately 3.8 volts versus Li/Li·. The reintercalation corresponds to approximately
30   101 milliamp hours per gram proportional to the intercalation of about 1.54 atomic units of lithium. The bottom of the curve corresponds to approximately 3.0 volts.

Figure 4 presents data obtained by multiple constant current cycling at 0.25 milliamp hours per square
35   centimeter of the $Li_3V_2(PO_4)_3$ versus lithium metal counter electrode between 3.0 and 4.2 volts using the electrolyte

and with electrodes formed as described earlier and with an initial specific capacity of 115 milliamp hours per gram. **Figure 4** is a two part graph with **Figure 4A** showing the excellent rechargeability of the $Li/Li_3V_2(PO_4)_3$ cell. **Figure**

5   **4B** shows good cycling and capacity of the cell. The performance shown after 113 cycles is good and shows that electrode formulations of the type $Li_3M'M''(PO_4)_3$ are very desirable.

It should be noted that the formulations obtained

10   by the method of the invention demonstrated capacity less than the achievable theoretical capacity. This is because the method of preparation and cell configurations have not yet been optimized for this remarkable material. Nevertheless, this material is highly desirable as an

15   active material to replace the widely used $LiMn_2O_4$, Li_1CoO_2, and $LiNiO_2$, as can be seen by considering its theoretical capacity. The theoretical specific capacity for $Li_3V_2(PO_4)_3$ is about 190 milliamp hours per gram. This is based on extracting all 3 lithium from the original starting

20   material. Actually, the theoretical capacity is closer to about 197 milliamp hours per gram corresponding to about 66 milliamp hours for each atomic unit of lithium extracted from the $Li_3V_2(PO_4)_3$ compound. Assuming that each such extracted unit of lithium corresponds to 66 milliamp hours,

25   it can be seen that in **Figure 1** the charge extracted of 136 milliamp hours per gram corresponds to the extraction of slightly more than 2 units of lithium from the $Li_2V_2(PO_4)_3$.

Example III (Hexagonal $Li_3AlV(PO_4)_3$)

30   A method for making $Li_3AlV(PO_4)_3$ will now be described. The basic procedure comprises conducting a reaction between lithium carbonate, aluminum hydroxide, vanadium oxide, and ammonium phosphate according to the reaction below.

35

$$3/2 \ Li_2CO_3 + Al(OH)_3 + 1/2 \ V_2O_3 + 3(NH_4H_2PO_4)$$

28

$$\rightarrow Li_3AlV(PO_4)_3 + 3 NH_3 + 6H_2O + 3/2 CO_2$$
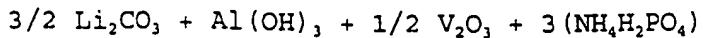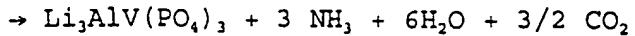
The precursor materials were initially intimately mixed and ground as described with respect to Example 1.

5   After mixing, the mixed precursor powders were compressed into tablet form and then heated at about 250°C for about 6 hours under an argon atmosphere. Then the temperature was raised to 600°C where heating was conducted for 12 hours, also under argon. Next, the pellets were cooled,

10   ground and repelletized. Next, heating was conducted for about 15 hours at a temperature of about 940°C under argon atmosphere.

The final product was subjected to CuK alpha X-ray diffraction as described with respect to Example 1.

15   The unit cell parameters are as described in Table H.

The chemical analysis and X-ray pattern demonstrated that the product of the invention was indeed the nominal general formula $Li_3AlV(PO_4)_3$.

20   Example IV

The $Li_3AlV(PO_4)_3$ prepared as described immediately above, was tested in an electrochemical cell, the positive electrode was prepared as described under the section designated "positive electrode." The negative electrode

25   was metallic lithium. The cell was prepared and cycled as generally described with respect to Example II above.

Figure 7 shows a voltage profile of the test cell based on the electrochemical voltage spectroscopy (EVS) technique, as described with respect to Example II above.

30   Figure 7 clearly shows and highlights the very high and unexpected degree of reversibility of lithium ion reactions of this compound. As in the case of Examples I and II, the material as prepared, is capable of first deintercalating lithium and then reintercalating lithium for functioning

35   reversibly in an ion cell. Figure 8 is an EVS differential capacity plot based on Figure 7. As can be seen from

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Figure 8, the relatively symmetrical nature of the peaks
indicates good electrochemical reversibility.

Figure 9 shows the results of the first constant
current cycling at plus/minus 0.05 milliamps per square
centimeter between about 3 and 4.5 volts based on the Li_{3-x}
$AlV(PO_4)_3$ active material in the cathode (positive
electrode). In an as-prepared, as-assembled initial
condition, the positive electrode active material contains
3 lithium, most being capable of deintercalation. The
lithium is deintercalated from the material during charging
of the cell. This material demonstrated about 35 milliamp
hours per gram when removing about 0.5 lithium per formula
unit per cycle. It was possible to reintercalate all of
the lithium which had been previously taken out in the
first half cycle.

Figure 10 shows data obtained by multiple
constant current cycling at plus/minus 0.05 milliamps per
square centimeter versus metallic lithium counter-
electrode. This graph shows good reversible cycling over
eight cycles. This demonstrates good cycling and capacity
of the cell.

Example V

The electrode material prepared in accordance
with Example 1 was tested in an electrochemical cell
against a negative electrode which was a carbon active
material designated MCMB2528. MCMB2528 is a mesocarbon
microbead material supplied by Alumina Trading, which is
the U.S. distributor for the supplier, Osaka Gas Company of
Japan. This material has a density of about 2.24 grams per
cubic centimeter; a particle size maximum for at least 95%
by weight of the particles of 37 microns; median size of
about 22.5 microns and an interlayer distance of about
0.336. Figure 11 shows results similar to that described
with respect to Examples I and II. In an as-prepared, as-
assembled initial condition, the positive electrode active

material is $Li_3V_2(PO_4)_3$. The lithium is deintercalated from
this active material during charging of the cell. During
charging, lithium is removed from the lithium vanadium
phosphate and intercalated into the MCMB carbon material.
Here, the positive electrode and negative electrode active
materials were not optimized. There was not a sufficient
quantity of the lithium vanadium phosphate to balance the
amount of carbon material in the negative electrode. Yet,
the cathode utilization was surprisingly good. **Figure 11**
shows that about 120 milliamp hours per gram was extracted
from the positive electrode material of the invention and
about 95 milliamp hours per gram was observed on first
discharge. This indicates that essentially all of the
lithium extracted from the lithium vanadium phosphate was
able to be reinserted in the second part of the cycle.

Figure 12 presents data obtained by multiple
constant current cycling at about plus/minus 0.2 milliamps
per square centimeter of the lithium vanadium phosphate of
Example 1 versus the MCMB carbon negative electrode,
between about 2.5 and 4.1 volts. **Figure 12** shows excellent
rechargability of the carbon/$Li_3V_2(PO_4)_3$ cell; with
performance through 10 cycles being very good.

Example VI

A material of the general formula $Li_3MnZr(PO_4)_3$
was prepared from the precursors lithium carbonate,
manganese oxide, zirconium oxide, and the ammonium
dihydrogen phosphate. This reaction was conducted in
accordance with the reaction shown below.

$$3/2\ Li_2CO_3 + MnO + ZrO_2 + 3\ (NH_4H_2PO_4)$$
$$\rightarrow Li_3\ Zr\ Mn(PO_4)_3 + 3NH_3 + 9/2\ H_2O + 3/2\ CO_2$$
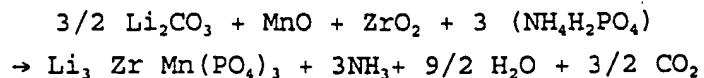
The procedure was followed similar to that
described with respect to Example III. The precursor
powders were mixed and then pelletized. They were then

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heated for about 6 hours at temperature of about 250°C under argon. Next, the temperature was elevated to 600°C and heating was conducted for about 12 hours under argon. The pellets were permitted to cool and then they were

5   ground and repelletized. Then heating was conducted for another 15 hours at a temperature of about 940°C under argon.

This procedure is similar to that described for the analogous sodium compounds $Na_3MnZr(PO_4)_3$, $Na_3MgZr(PO_4)_3$

10 as reported by Feltz and Barth in Solid State Ionics 9-10 (1983) pp. 817-822. These compounds may be prepared by the method described by Feltz and Barth in the sodium form and the lithium form is prepared by ion substitution by well known methods. Direct preparation using lithium precursors

15 as described above, and consistent with the methods of Feltz and Barth, is preferred. However, it should be noted that the preparation methods of Feltz and Barth are conducted in an air atmosphere. The effects of the atmosphere on the product characteristics are described

20 below. Such relationship is based on the data given above in the examples related to hydrogen and argon atmosphere. Another example using hydrogen atmosphere follows immediately below.

25 <u>Example VII (Orthorhombic $Li_3AlV(PO_4)_3$)</u>

The procedure for forming the orthorhombic $Li_3AlV(PO_4)_3$ was generally as per Example III, except that a different atmosphere was used for the heating steps and the vanadium oxide precursor differed. The reaction was as

30 given below.

$$3/2 \ Li_2CO_3 + Al(OH)_3 + 1/2 \ V_2O_5 + 3(NH_4H_2PO_4)$$
$$\rightarrow Li_3AlV(PO_4)_3 + 3 \ NH_3 + 6H_2O + 3/2 \ CO_2$$
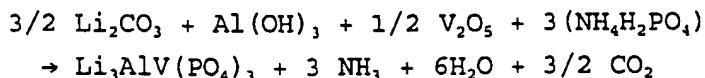
35 Here, V_2O_5 was used in place of the V_2O_3 of Example III. All heating steps in this Example VII were

32

carried out under H$_2$ (hydrogen) gas atmosphere. Essentially 100% H$_2$ atmosphere was achieved using flowing H$_2$ gas. The product of this Example VII (orthorhombic) had different structure and electrochemical performance as

5   compared to Example III (hexagonal). See Table I for unit cell parameters obtained by CuK-alpha x-ray diffraction.

Example VIII

The Li$_3$AlV(PO$_4$)$_3$ prepared as per Example VII

10   above, was tested in an electrochemical cell, the positive electrode was prepared as described under the section designated "positive electrode." The negative electrode was metallic lithium. The cell was prepared and cycled as generally described with respect to Example II above.

15   Figure 13 shows a voltage profile of the test cell based on the electrochemical voltage spectroscopy (EVS) technique, as described with respect to Example II above. Figure 13 clearly shows a very high degree of reversibility of lithium ion reactions of this orthorhombic

20   structure. The material as prepared, is capable of first deintercalating lithium and then reintercalating lithium for functioning reversibly in an ion cell. Figure 14 is an EVS differential capacity plot based on Figure 13. Figure 14 shows a profile different from the hexagonal form of

25   this compound as per Figure 8.

Figure 15 shows the results of the first constant current cycling at plus/minus 0.05 milliamps per square centimeter between about 3 and 4.2 volts based on the Li$_{3-x}$AlV(PO$_4$)$_3$ active material in the cathode (positive

30   electrode). This material demonstrated about 55 milliamp hours per gram, and permitted removing more lithium per cycle than the product of Example III.

A comparison of Figures 9 and 15 reveals that the orthorhombic Li$_3$AlV(PO$_4$)$_3$ (Fig. 15) had better performance,

35   higher specific capacity, i.e., better cathode utilization

than the hexagonal $Li_3AlV(PO_4)_3$ of Fig. 9. Recall that the $Li_3AlV(PO_4)_3$ of Fig. 9 was prepared under argon using V_2O_3 and the $Li_3AlV(PO_4)_3$ of Fig. 15 was prepared under H_2 gas using V_2O_5. In the latter process, V_2O_5 is thought to be

5   reduced in situ to V_2O_3 under hydrogen.

        The benefits of the H_2 gas atmosphere, a reducing atmosphere, were also observed in the preparation of the $Li_3V_2(PO_4)_3$ when compared to the same product prepared under argon. The argon-prepared $Li_3V_2(PO_4)_3$ originated from a V_2O_3

10   precursor and had first charge-discharge cycle specific capacity of 105 mAh/g out (lithium extracted) and 80 mAh/g in (lithium inserted). The H_2-prepared $Li_3V_2(PO_4)_3$ originated from a V_2O_5 precursor and had first charge-discharge cycle specific capacity of 136 mAh/g out (lithium

15   extracted) and 131 mAh/g in (lithium inserted) as per Examples I and II.

        There is no known prior attempt to deintercalate lithium from a lithium-containing metal phosphate. Thus, the electrochemical reaction demonstrated by the present

20   invention is remarkable as it has not heretofore been suggested. The product of the present invention may be compared to a Nasicon $(Na_3Zr_2PSi_2O_{12})$ framework which is a skeleton structure with an interconnected interstitial space. There are also the Langbeinite-type $(K_2Mg_2(SO_4)_3)$

25   structures which are true cage structures. Such structures do not permit mobility of mobile metal ions through the crystal. Some Nasicon-type structures possess ionic conductivity but have very poor electronic conductivity. Some Nasicon-type structures are usable as solid

30   electrolytes, but are not usable as electrode materials. This is because they lack an oxidizable metal in their structure, therefore, an ion cannot be extracted. Thus, such structures and compounds are useless for ion battery, rocking chair battery, application.

35   In contrast to the known art, the present invention provides a lithium-metal-phosphate compound

having an oxidizable metal. Such metal is capable of more than one oxidation state. The metal is present in the lithium-metal-phosphate compound at less than its highest oxidation state. Therefore, the metal is oxidizable to

5   provide capability to extract out one or more Li^+ ions. This is demonstrated by oxidation of V in $Li_3V_2(PO_4)_3$ from $V^{+3}V^{+3}$ to $V^{+4}V^{+5}$. It should be noted that based on formation as described herein, there are many combinations. See Tables $\underline{A}$ to $\underline{I}$. The oxidation states for many compounds of

10   the invention are as per the examples and tables. Note that the amount of Li^+ removed or added will determine the relative oxidation state of E' and E" or M' and M". For example, Fe in $Li_3Fe_2(PO_4)_3$ from $Fe^{+3}Fe^{+3}$ to $Fe^{+4}Fe^{+4}$; Mn in $Li_3Mn_2(PO_4)_3$ from $Mn^{+3}Mn^{+3}$ to $Mn^{+4}Mn^{+4}$; and other $Li_3M_1M_2(PO_4)_3$

15   as per $Fe^{+3}Ti^{+3}$ to $Fe^{+4}Ti^{+4}$; $Co^{+3}Mn^{+3}$ to $Co^{+4}Mn^{+4}$; $Cu^{+2}Mn^{+4}$ to $Cu^{+3}Mn^{+4}$, and $Fe^{+3}V^{+3}$ to $Fe^{+4}V^{+4}$.

Table A.

$Li_{3-x}M'M''(PO_4)_3$

M' = Non transition metal initial oxidation state = +3

M" = Transition metal initial oxidation state = +3

M'M"	RMM	No. of Li's Removed	mAh/g
Al Ti	381	1	70
Al V	384	2	140
Al Cr	385	3	209
Al Mn	388	1	69
Al Fe	389	1	69
Al Co	392	1	68
Al Ni	392	1	68
Al Cu	397	1	68
B Ti	365	1	73
B V	368	2	146
B Cr	369	3	218
B Mn	372	1	72
B Fe	373	1	72
B Co	376	1	71
B Ni	376	1	71
B Cu	381	1	70

Note: Refer to footnotes 3 and 4 of Table C

36

Table B. $Li_{3-x} M'M'' (PO_4)_3$

M' = Non transition metal initial oxidation state = +2

M"= Transition metal initial oxidation state = +4

M'M"	RMM	No. of Li's Removed	mAh/g
Mg V	381	1	70
Mg Mo	426	2	126
Mg Cr	382	2	140
Ca V	397	1	68
Ca Mo	442	2	121
Ca Cr	398	2	135

Note: Refer to footnotes 3 and 4 of Table C

Table C. $Li_{3-x} M^{II} M^{IV} (PO_4)_3$

M^{IV} = Zr, Ti

M^{II} = Any transition metal capable of +2 oxidation state

M^{II} [1] Ionic radius	$M^{II} M^{IV}$ [2]	RMM	No. of Li's Removed	mAh/g
67 pm	Mn Zr	452	2	119
86 pm	Ti Zr	445	2	120
79 pm	V Zr	448	3	180
80 pm	Cr Zr	449	3	179
78 pm	Fe Zr	453	2	118
74 pm	Co Zr	456	2	118
69 pm	Ni Zr	456	2	118
73 pm	Cu Zr	461	1	58
69 pm	Mo Zr	493	3	163
67 pm	Mn Ti	409	2	131
86 pm	Ti Ti	402	2	133
79 pm	V Ti	405	3	199
80 pm	Cr Ti	406	3	199
78 pm	Fe Ti	410	2	131
74 pm	Co Ti	413	2	130
69 pm	Ni Ti	413	2	130
73 pm	Cu Ti	418	1	64
69 pm	Mo Ti	450	3	178

(1)   Taken from R.D. Shannon, Acta Cryst. A32, 751 (1976).

38

(2)   In each case the M^{II} oxidizes to higher
        oxidation state in proportion to the amount of
        Li removed, because the Zr^{IV} and the Ti^{IV} do not
        oxidize.

5

(3)   RMM is relative molecular mass.

(4)   The term "No. of Li's Removed" is on a per
        formula unit basis.

10

Table D. $Li_{3-x}Sn^{II}M^{IV}(PO_4)_3$

M^{IV} = Transition metal oxidation state = +4

Sn M^{IV}	RMM	No. of Li's Removed	Oxidations	mAh/g
Sn V	476	3	$Sn^{2+} \rightarrow Sn^{4+}$ $V^{4+} \rightarrow V^{5+}$	169
Sn Cr	477	3	$Sn^{2+} \rightarrow Sn^{4+}$ $Cr^{4+} \rightarrow Cr^{5+}$	169
Sn Mo	521	3	$Sn^{2+} \rightarrow Sn^{4+}$ $Mo^{4+} \rightarrow Mo^{5+}$	154

Note: Refer to footnotes 3 and 4 of Table C.

The designation of oxidation pertains to expected performance based on analogy to corresponding results achieved as per the Examples.

Table E. $Li_{3-x} Pb^{II} M^{IV} (PO_4)_3$

	RMM	Li's Removed	Oxidations	mAh/g
PbV	564	3	$Pb^{2+} \rightarrow Pb^{4+}$	143
			$V^{4+} \rightarrow V^{5+}$	
PbCr	565	3	$Cr^{4+} \rightarrow Cr^{5+}$	
			$Pb^{2+} \rightarrow Pb^{4+}$	142
PbMo	609	3	$Pb^{2+} \rightarrow Pb^{4+}$	132
			$Mo^{4+} \rightarrow Mo^{5+}$	

5

Note: Refer to all footnotes of Table D.

Table F. $Li_{3-x}SnM^{IV}(PO_4)_3$

M^{IV} = Zr, Ti

		RMM	Li's Removed	Oxidation	mAh/g
5	SnZr	516	2	$Sn^{2+} \to Sn^{4+}$	104
	SnTi	473	2	$Sn^{2+} \to Sn^{4+}$	113

10

Table G. $Li_{3-x}PbM^{IV}(PO_4)_3$

		RMM	Li's Removed	Oxidation	mAh/g
15					
	PbZr	604	2	$Pb^{2+} \to PB^{4+}$	89
	PbTi	561	2	$Pb^{2+} \to PB^{4+}$	96

20

Note: Refer to all footnotes of Table D.

Table H. Li₃AlV(PO₄)₃

Li₃AlV(PO₄)₃ Fit to a Hexagonal Unit Cell

A = 9.383871   .034458 A   Alpha = 90.000000 Degrees

5   B = 9.383871   .034458 A   Beta = 90.000000 Degrees

C = 24.841420   .118174 A   Gamma = 120.000000 Degrees

Unit cell volume = 1894.40 cubic angstroms

H	K	L	SST-OBS	SST-CALC
1	0	2	.012937	.012831
1	1	0	.026589	.026953
1	1	2	.031495	.030800
0	0	6	.034983	.034615
2	0	2	.040351	.039784
0	0	7	.047178	.047115
2	0	4	.051993	.051323
1	0	7	.055883	.056100
2	1	0	.063080	.062891
2	1	2	.065955	.066738
1	0	9	.085993	.086869

Table I. $Li_3AlV(PO_4)_3$

$Li_3AlV(PO_4)_3$ Fit to an Orthorhombic Unit Cell

5   A = 7.947642   .004678 A   Alpha =   90.000000 Degrees

        B = 21.493340   .012984 A   Beta   =   90.000000 Degrees

        C =   6.983464   .004729 A   Gamma = 90.000000 Degrees

Unit cell volume = 1185.24 cubic angstroms

	H	K	L	SST-OBS	SST-CALC
10	1	3	0	.020869	.020954
	1	3	1	.033500	.033279
	2	0	0	.037402	.037575
				.040448	
	1	5	0	.041766	.041505
15	0	6	0	.046122	.046240
	0	2	2	.054563	.054438
	2	4	0	.058276	.058126
	0	6	1		.058565
				.066397	
20	1	6	1	.067686	.067958
	2	4	1	.070720	.070451
	1	4	2	.079475	.079245
	2	6	0	.083848	.083815
	2	0	2	.086672	.086876
25	0	6	2	.095410	.095540
	2	7	0	.100296	.100512
	0	1	3		.112211
	0	7	2	.112303	.112238
	1	9	0	.113604	.113433
30				.124763	
	3	3	2	.145561	.145405
	0	6	3	.156832	.157166
	3	5	2		.165956
	2	10	0	.166092	.166018
35	1	6	3		.166560
	0	8	3	.193220	.193130
	1	3	4	.218344	.218156

Lithium ion batteries made with this technology are made
in the discharged state, also referred to as pre-charge
(before charge) state. They require a conditioning
charge before use. In the initial condition (pre-charge
5   state), anodes of lithium ion batteries are essentially
free of lithium, and often free of ions thereof, as in
the case of graphite. Therefore, such batteries, in the
initial condition (as-assembled) pre-charge state, are
inherently more stable and relatively less reactive than
10   batteries containing lithium metal, or containing fully
or partially charged anodes. The active materials
themselves are also inherently air stable.

   To achieve a useable potential difference, the
(positive electrode) is electrochemically oxidized, while
15   the anode (negative electrode) is reduced. Thus, during
charging, a quantity (x) of lithium ions (Li^+) leave the
positive electrode, $Li_{3-x}M'_yM''_{2-y}(PO_4)_3$, and the positive
electrode is oxidized, increasing its potential; during
charging, the Li ions are accepted at or intercalated
20   into a negative electrode, preferably a carbon-based
negative electrode, which is reduced. As a result, the
negative electrode has a potential very close to the
lithium metal potential, which is zero volts. A typical
graphite electrode can intercalate up to about 1 atom of
25   lithium per each of 6 carbons, that is, Li_0C_6 to Li_1C_6.
During discharging, the reverse occurs, and a quantity of
(x) of lithium (Li^+) ions leave the negative electrode,
increasing its potential. During discharge, the lithium
ions are accepted (intercalated) back into the positive
30   electrode, which is reduced, and its potential is
reduced. If the $Li_3M'_yM''_{2-y}(PO_4)_3$ compound were used as a
negative electrode, during charge, Li ions would be
transferred to the negative electrode, as $Li_{3+x}M_yM_{2-y}(PO_4)_3$
and the M', M", or both, would theoretically achieve a
35   higher oxidation state. On discharge, the Li^+ ions would
be transferred back to the positive electrode.

45

The compounds of the invention are also
characterized by being air stable in an as-prepared
condition. This is a striking advantage, because it
facilitates preparation of and assembly of battery

5   cathodes and cells, without the requirement for
controlled atmosphere. This feature is particularly
important, as those skilled in the art will recognize
that air stability, that is, lack of degradation on
exposure to air, is very important for commercial

10   processing. Air-stability is known in the art to more
specifically indicate that a material does not hydrolyze
in presence of moist air. Generally, air-stable
materials are also characterized by extracting Li above
about 3.0 volts versus lithium. The higher the

15   extraction potential, the more tightly bound the lithium
ions are to the host lattice. This tightly bound
property generally confers air stability on the material.
The air-stability of the $Li_3M'M''(PO_4)_3$ materials of the
invention is consistent with the stability demonstrated

20   for $Li_3V_2(PO_4)_3$ by constant current cycling at 0.20
milliamps per square centimeter between about 3 and 4.2
volts versus Li metal anode. If a material intercalates
Li below about 3.0 volts versus lithium, it is generally
not air-stable, and it hydrolyzes in moist air.

25   While this invention has been described in
terms of certain embodiments thereof, it is not intended
that it be limited to the above description, but rather
only to the extent set forth in the following claims.
          The embodiments of the invention in which an

30   exclusive property or privilege is claimed are defined in
the following claims.

Claims:

1.   A lithium ion battery comprising: a first
electrode having an active material in a first condition
of the nominal general formula $Li_{3-x}M'_yM''_{2-y}(PO_4)_3$, x =
0, $0 \le y \le 2$, and in a second condition of the nominal
general formula $Li_{3-x}M'_yM''_{2-y}(PO_4)_3$, $0 < x \le 3$; M'' is a
transition metal, and M' is a non-transition-metal
element selected from the group consisting of metals and
metalloids; a second electrode which is a counter-
electrode to said first electrode; and an electrolyte
between said electrodes.

2.   The battery of claim 1 wherein M' is
selected from the group consisting of Mg, Be, Ca, Sn, Pb,
Ge, B, K, Al, Ga, In, As, and Sb.

3.   The battery of claim 1 wherein M'' is
selected from the group consisting of Ti, V, Cr, Mn, Fe,
Co, Ni, Cu, Mo, W, Zn, Cd, and Pd.

4.   A lithium ion battery comprising: a first
electrode having an active material in a first condition
of the nominal general formula $Li_{3-x}M'_yM''_{2-y}(PO_4)_3$, x =
0, $0 \le y \le 2$, and in a second condition of the nominal
general formula $Li_{3-x}M'_yM''_{2-y}(PO_4)_3$, $0 < x \le 3$; M' is Zr or
Ti; and M'' is a metal characterized by having a +2
oxidation state when x = 0; a second electrode which is a
counter-electrode to said first electrode; and an
electrolyte between said electrodes.

5.   The battery of claim 4 wherein said Zr or
Ti has a +4 oxidation state in said compound,
corresponding   to $Li_{(3-x)}M_y{}^{IV}M_{(2-y)}{}^{II}(PO_4)_3$.

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6.　　The battery of claim 4 wherein M" is a transition metal.

7.　　The battery of claim 4 wherein M" is selected from the group consisting of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Sn, Pb, Mo, W, and Pd.

8.　　The battery of claim 4 wherein said second electrode active material is selected from the group consisting of carbon, graphite, and mixtures thereof.

9.　　A lithium ion battery which comprises a positive electrode and a negative electrode; said negative electrode comprising an active material consisting of an intercalation material in a pre-charge state; said positive electrode having an active material comprising a phosphorous compound of the nominal general formula $Li_3M'_yM"_{2-y}(PO_4)_3$, $y \le 0 \le 2$,; wherein M' and M" are the same or different from one another and are each elements selected from the group consisting of metals and metalloids; and wherein said compound deintercalates lithium ions during charging cycle of said battery; said negative electrode active material characterized by intercalating said deintercalated lithium ions during said charging cycle and by subsequent deintercalation of lithium ions during discharge cycle; and said compound characterized by reintercalating said discharge cycle lithium ions.

10.　　The battery of claim 9 wherein M" is a transition metal.

11.　　The battery of claim 9 wherein M" is a transition metal, and M' is a non-transition-metal metal,

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12.   The battery of claim 9 wherein M' is
selected from the group consisting of Mg, Be, Ca, Sn, Pb,
Ge, B, K, Al, Ga, In, As, and Sb.

13.   The battery of claim 9 wherein M" is
selected from the group consisting of Ti, V, Cr, Mn, Fe,
Co, Ni, Cu, Mo, W, Zn, Cd, and Pd.

14.   The battery of claim 9 wherein M' is Zr or
Ti; and M" is a metal characterized by having a +2
oxidation state.

15.   The battery of claim 14 wherein said Zr or
Ti has a +4 oxidation state in said compound,
corresponding to $Li_{3-x}M_y{}^{IV}M_{(2-y)}{}^{II}(PO_4)_3$; and said M" is a
transition metal.

16.   The battery of claim 9 wherein said second
electrode active material is a carbonaceous material.

17.   The battery of claim 9 wherein said second
electrode active material is selected from the group
consisting of carbon, graphite, and mixtures thereof.

18.   The battery of claim 9 wherein, during
charging cycle of said battery, the oxidation state of at
least one of said M' and M" in said compound increases in
relation to said lithium ions (x) deintercalated from
said compound during said charging cycle, $0 < x \le 3$.

19.   A method of chemically preparing a product
of the nominal formula $Li_3M'_yM"_{2-y}(PO_4)_3$, $0 \le y \le 2$ where M'
and M" are each independently selected from the group of
metals, comprising the steps of:
     a.   intermingling particles of at least
       one metal oxide compound, particles

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of a lithium compound, and particles
of a phosphate salt compound, said
compounds being in a proportion which
provides said nominal formula
proportion; and

b. reacting said compounds in the
presence of a non-oxidizing
atmosphere to provide said product.

20. The method of claim 19 wherein said
phosphate salt compound is ammonium phosphate; said
lithium compound is lithium carbonate; said at least one
metal oxide compound includes V_2O_5 and; said non-
oxidizing atmosphere is a reducing atmosphere.

21. The method of claim 20 wherein said at
least one metal oxide compound includes V_2O_5 and $Al(OH)_3$;
and said reducing atmosphere comprises hydrogen gas.

22. The method of claim 19 wherein said
reacting step (b) is conducted by:

(i) heating to a first temperature
sufficient to decompose at least one
of said lithium compound and said
phosphate salt compound; and then
(ii) heating to a second temperature
sufficient to form said product and
less than the decomposition
temperature of said product.

23. The method of claim 22 wherein said first
temperature is in a range of about 550°C to about 750°C
and said second temperature is in a range of about 800°C
to about 1000°C.

50

24. The method of claim 22 wherein after step (b) (ii), said product is ground, and steps (b) (i) and (b) (ii) are repeated in sequence.
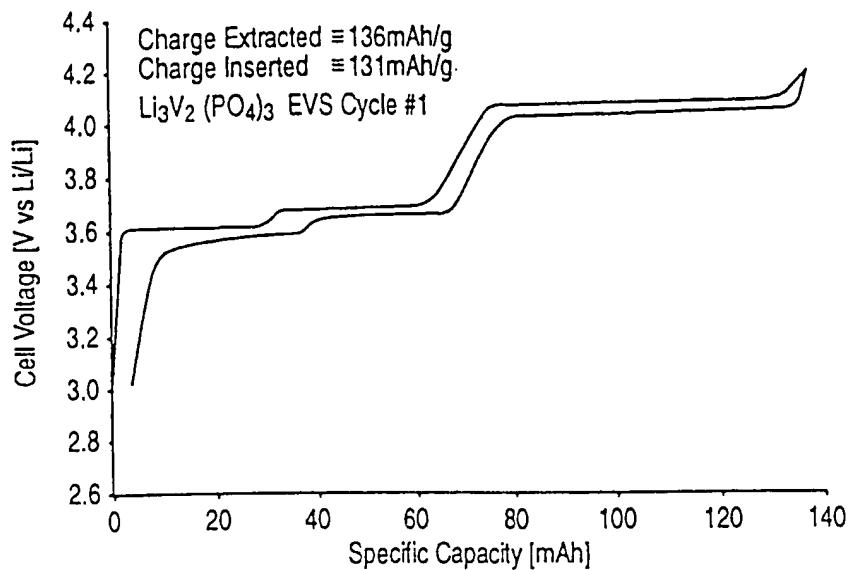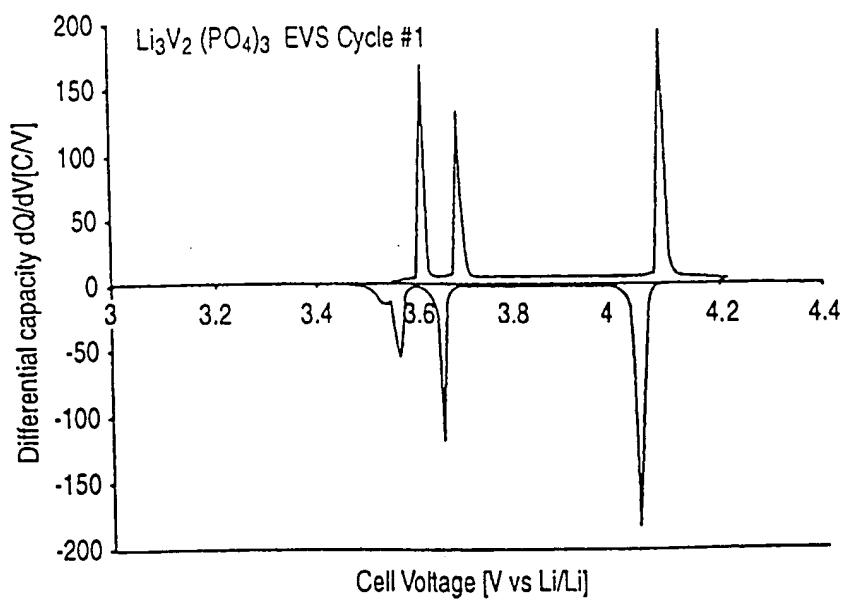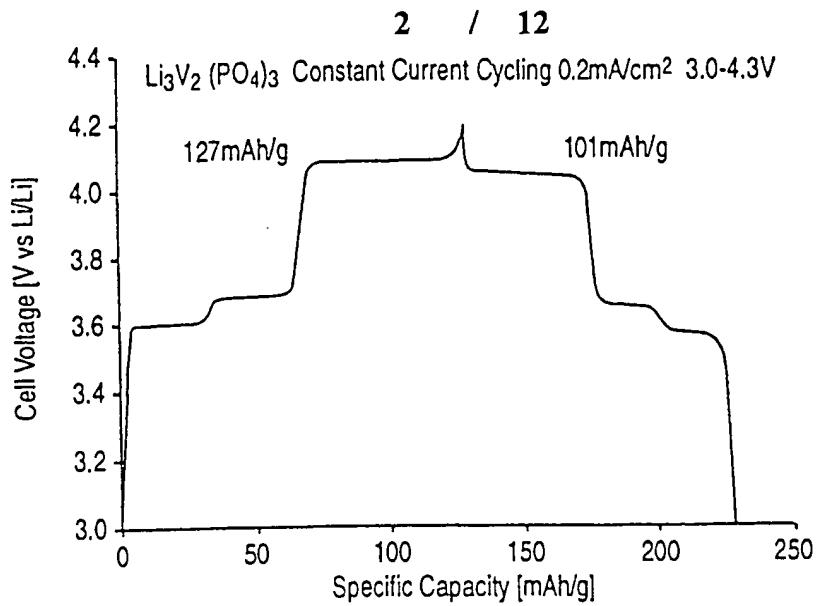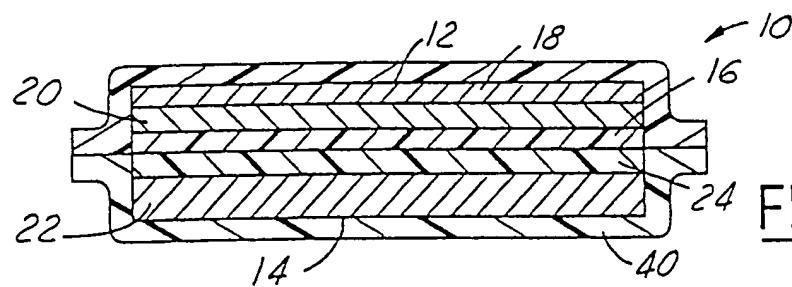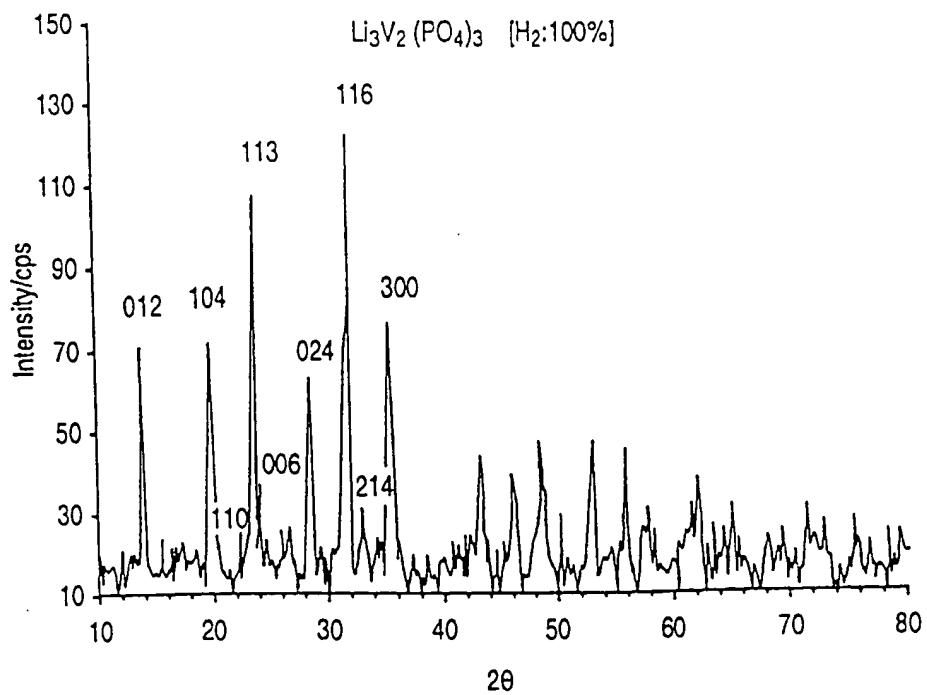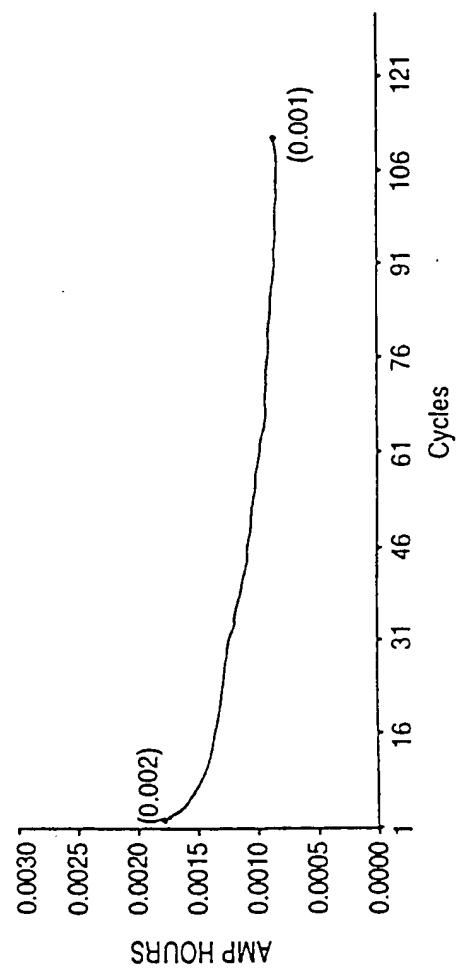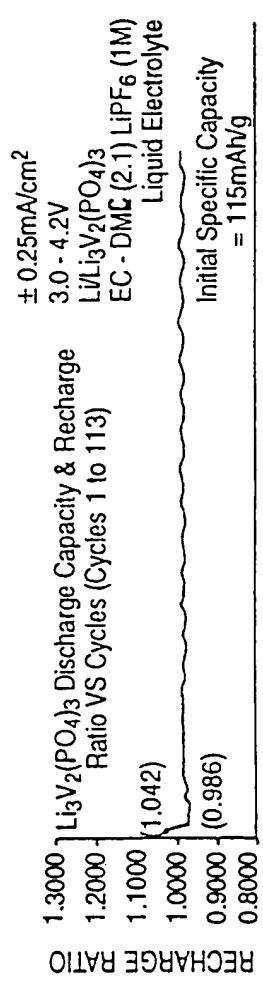
Charge Extracted ≡136mAh/g
Charge Inserted ≡131mAh/g

$Li_3V_2(PO_4)_3$ EVS Cycle #1

FIG.1

$Li_3V_2(PO_4)_3$ EVS Cycle #1

FIG.2

FIG.3

FIG.5

FIG.6

Li₃V₂(PO₄)₃ Discharge Capacity & Recharge
Ratio VS Cycles (Cycles 1 to 113)

± 0.25mA/cm²
3.0 - 4.2V
Li/Li₃V₂(PO₄)₃
EC - DMC (2.1) LiPF₆ (1M)
Liquid Electrolyte

Initial Specific Capacity
= 115mAh/g

(1.042)
(0.986)

RECHARGE RATIO

FIG. 4A

AMP HOURS

Cycles

(0.002)
(0.001)

FIG. 4B

Electrochemical Voltage Spectroscopy
Cell#502581 $Li_3AlV(PO_4)_3$ vs. Li

Cathode Specific Capacity [mAh/g]

Electrode Potential [V vs. Li/Li^+]

FIG.7

Electrochemical Voltage Spectroscopy
Cell#502581 $Li_3AlV(PO_4)_3$ vs. Li

Differential Capacity [dQ/dV]
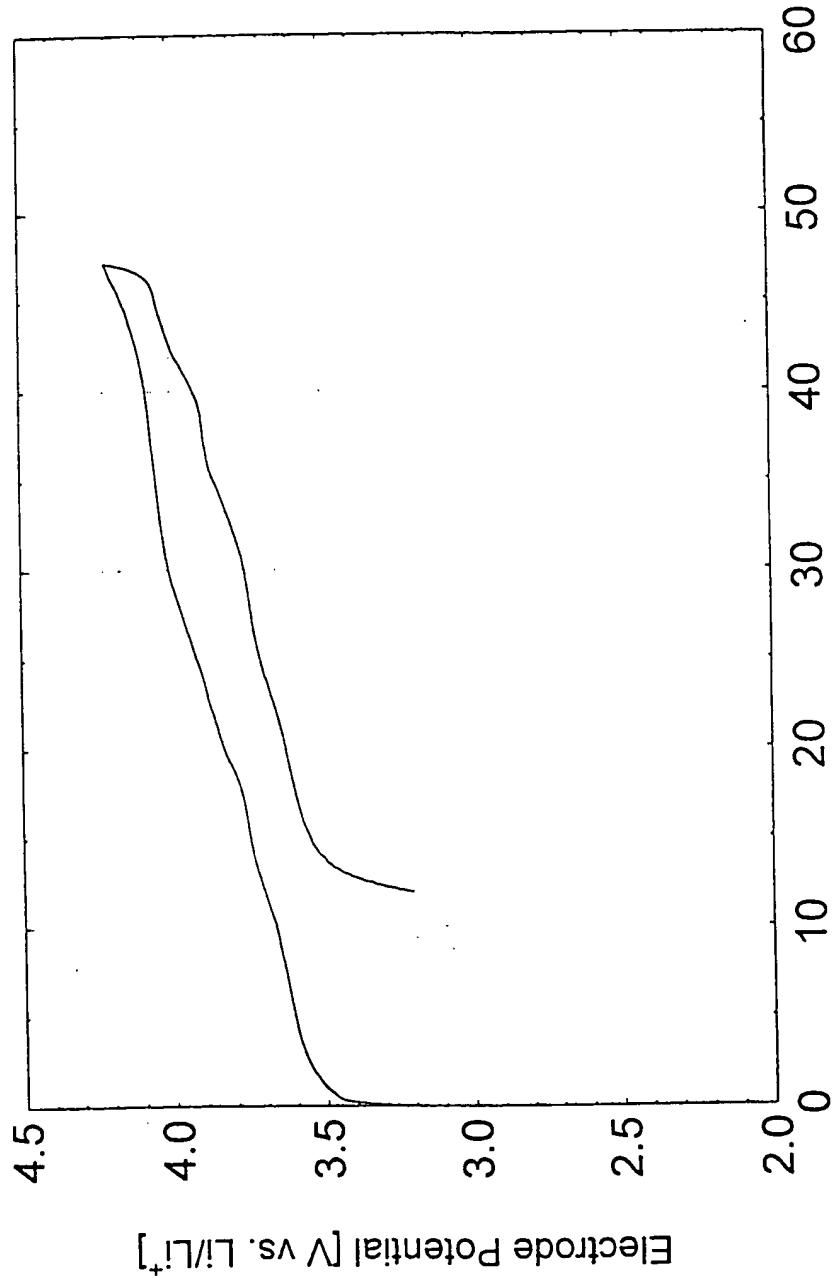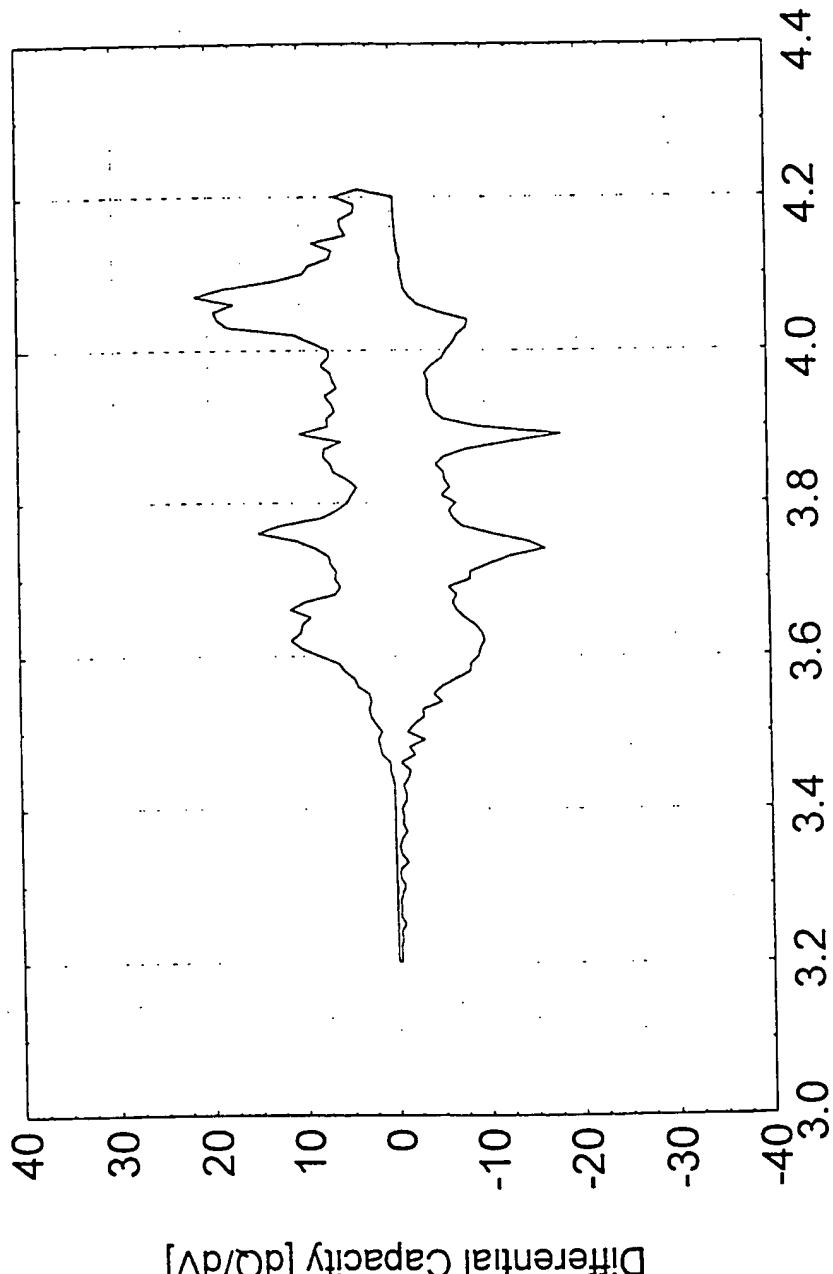
Electrode Potential [V vs Li/Li^+]

FIG.8

Cell#502577 Li/Li$_3$AlV(PO$_4$)$_3$
Cycle#1 ±0.05 mA/cm^2 3.0-4.5 V

Cathode Utilization
1st Charge 41 mAh/g
1st Discharge 32 mAh/g

Electrode Potential [V vs. Li/Li$^+$]

Cumulative Cathode Specific Capacity [mAh/g]

FIG.9

FIG.10

Cell#502577 Li/Li$_3$AlV(PO$_4$)$_3$
±0.05 mA/cm^2 3.0 - 4.5 V
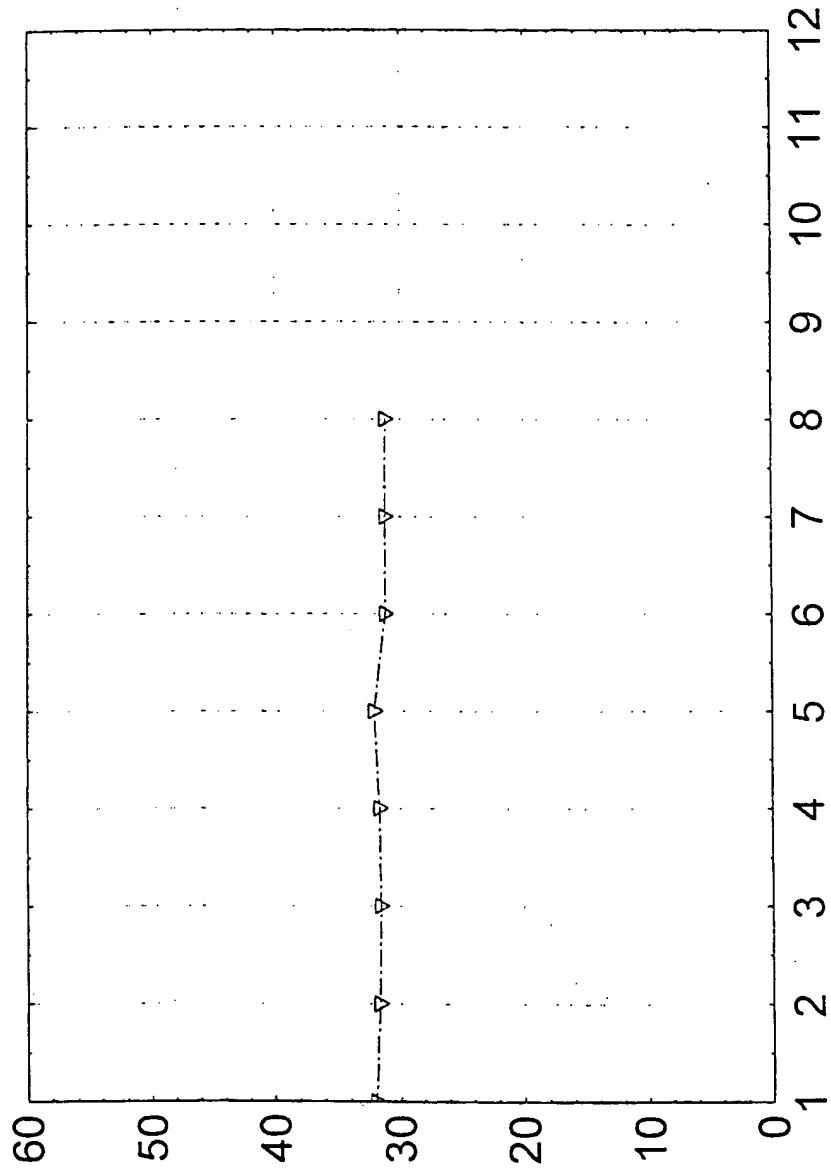
Cycle Number

Li$_3$AlV(PO$_4$)$_3$ Discharge Specific Capacity [mAh/g]

Cell#502582 MCMB2528/Li$_3$V$_2$(PO$_4$)$_3$

Cycle#1 ±0.2 mA/cm^2 2.5 - 4.1 V

Cathode Utilization
1st charge 120 mAh/g
1st discharge 95 mAh/g

Cell Voltage [V]

Cumulative Cathode Specific Capacity [mAh/g]

FIG.11

Cell#502582 MCMB2528/$Li_3V_2(PO_4)_3$

$\pm$0.2 mA/cm^2 2.5 - 4.1 V
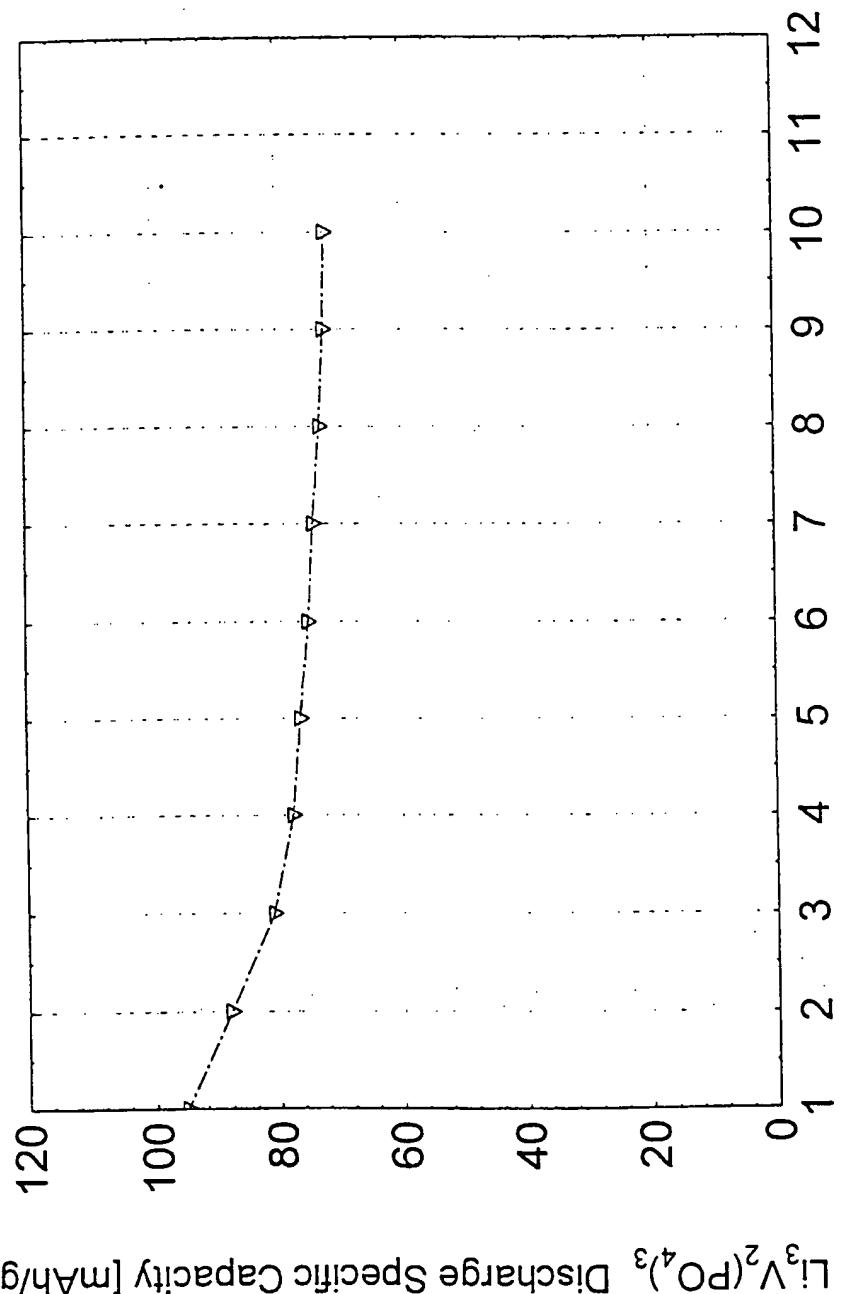
$Li_3V_2(PO_4)_3$ Discharge Specific Capacity [mAh/g]

Cycle Number

FIG.12

Electrochemical Voltage Spectroscopy
Cell#502653 $Li_3AlV(PO_4)_3$ (Prepared Under H_2 Ambient) vs. Li

Cathode Specific Capacity [mAh/g]

Electrode Potential [V vs. Li/Li$^+$]
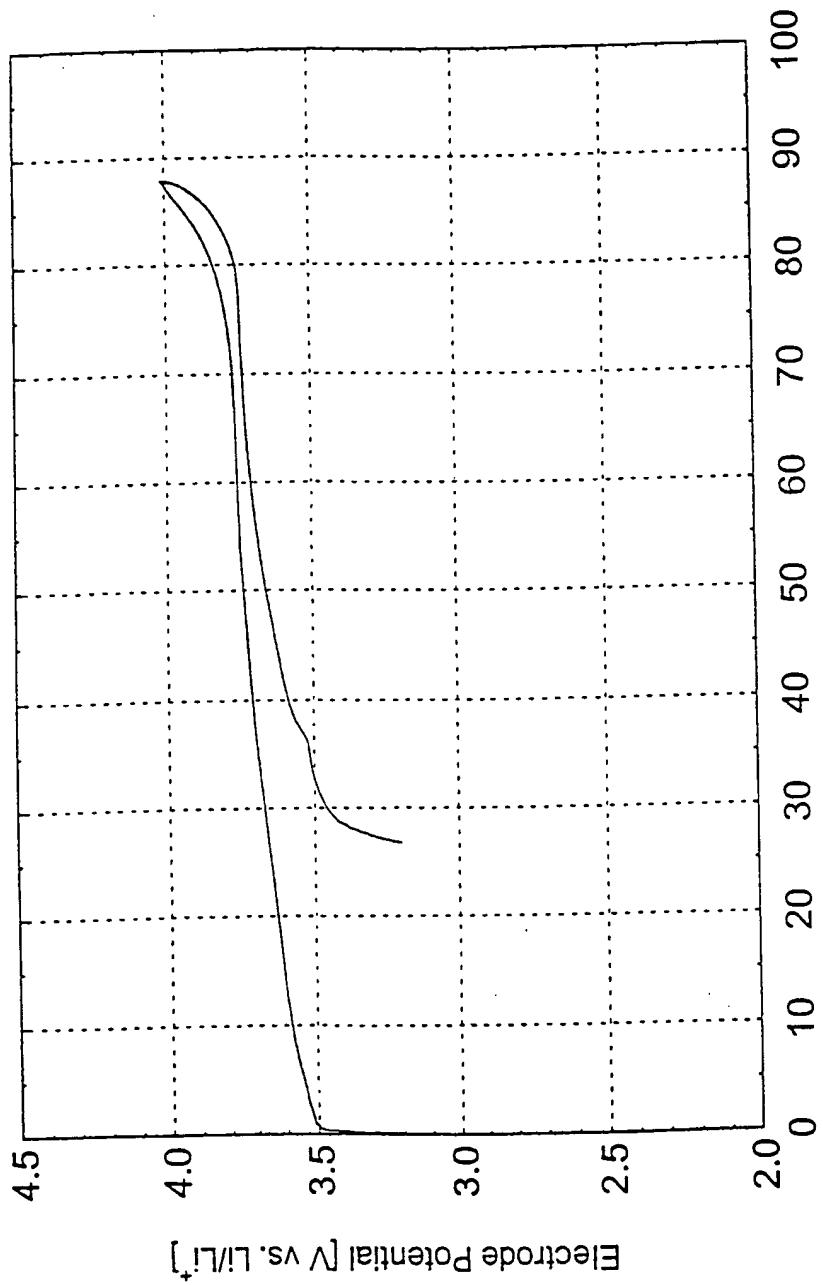
FIG. 13

Electrochemical Voltage Spectroscopy
Cell#502653 Li$_3$AlV(PO$_4$)$_3$ (Prepared Under H$_2$ Ambient) vs. Li

FIG. 14

Electrode Potential [V vs Li/Li$^+$]

Differential Capacity [dQ/dV]
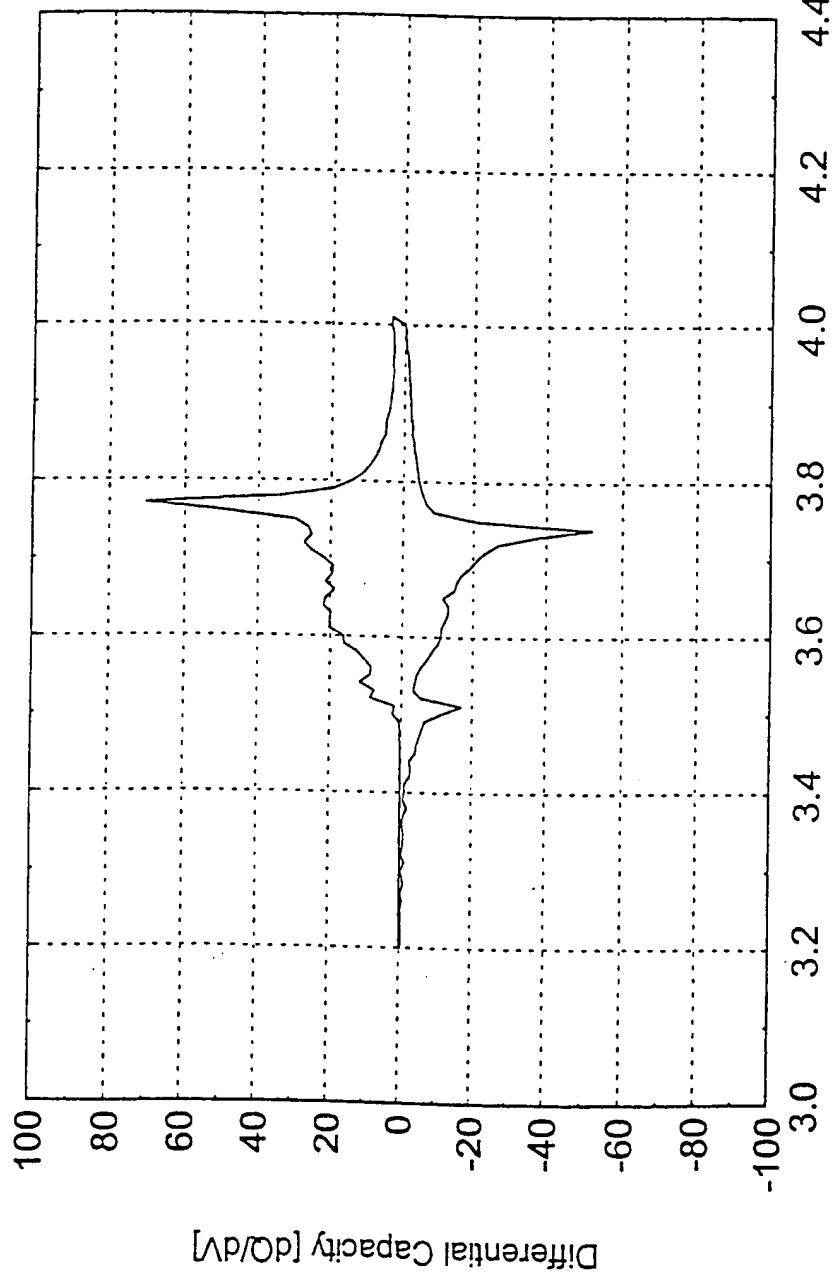
Cell#502650 Li/Li$_3$AlV(PO$_4$)$_3$ Prepared Under H$_2$ Ambient

Cycle#1 ±0.05 mA/cm^2 3.0-4.2 V
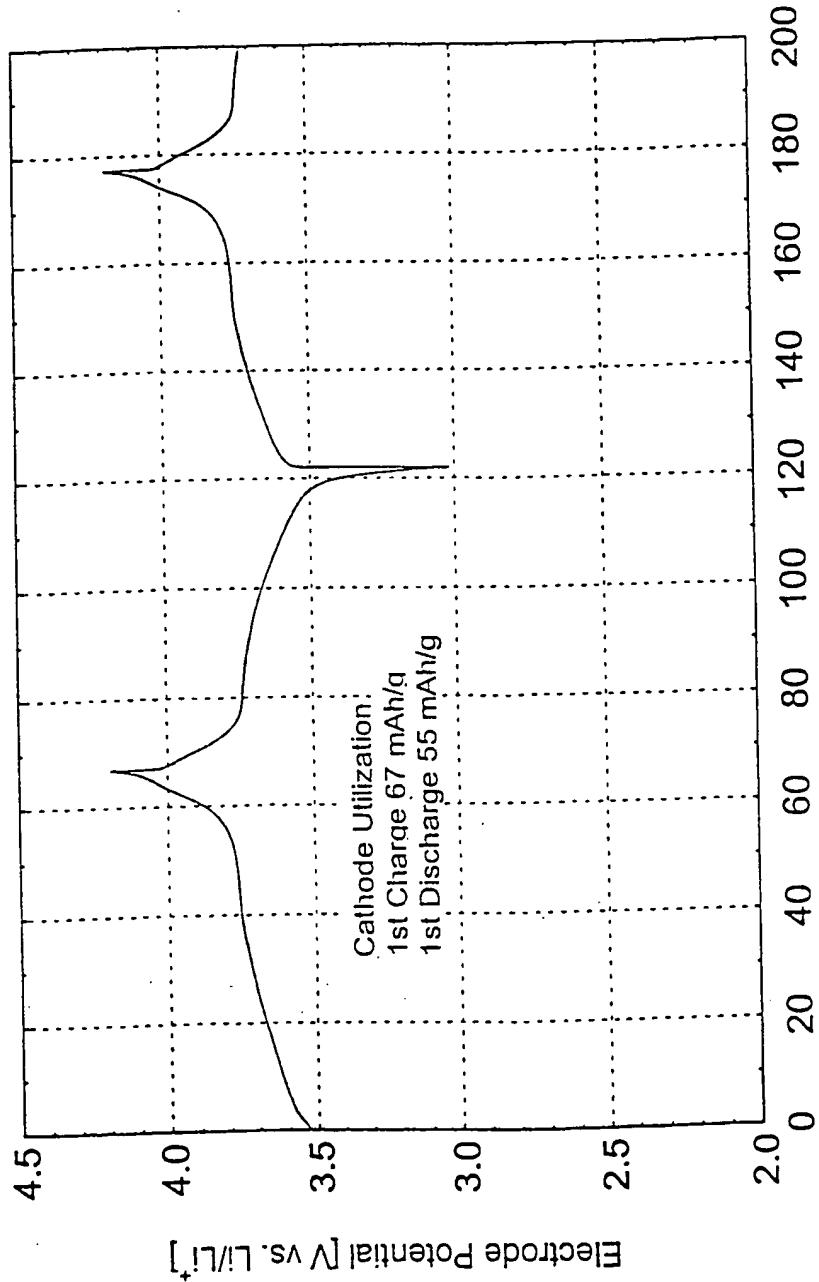
Cathode Utilization
1st Charge 67 mAh/g
1st Discharge 55 mAh/g

Cumulative Cathode Specific Capacity [mAh/g]

Electrode Potential [V vs. Li/Li$^+$]

FIG. 15

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7   H01M4/58   H01M10/40   C01B25/45

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7   H01M C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 12761 A (SAIDI MOHAMED YAZID ;BARKER JEREMY (US); VALENCE TECHNOLOGY INC (U) 26 March 1998 (1998-03-26) page 5, line 19 - line 20; claims 1,8,9,14; example 1 page 24, line 30 - line 35 page 14, line 31 - line 35 page 16, line 18 -page 17, line 24 page 18, line 5 - line 6	1-24
X	WO 97 40541 A (UNIV TEXAS) 30 October 1997 (1997-10-30) claims 6,8,11; example 1	1-19
A		20,22

-/—

[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
16 February 2000	24/02/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Andrews, M

3

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	DELMAS C ET AL: "THE NASICON-TYPE TITANIUM PHOSPHATES ATI2(PO4)3 (A=LI, NA) AS ELECTRODE MATERIALS" SOLID STATE IONICS,NL,NORTH HOLLAND PUB. COMPANY. AMSTERDAM, vol. 28 - 30, no. PART 01, 1 September 1988 (1988-09-01), pages 419-423, XP002048302 ISSN: 0167-2738 experimental, page 420	1,3-5, 8-10,13, 16-19, 22-24
X	DATABASE INSPEC 'Online! INSTITUTE OF ELECTRICAL ENGINEERS, STEVENAGE, GB PADHI A K ET AL: "Mapping of transition metal redox energies in phosphates with NASICON structure by lithium intercalation" Database accession no. 5693819 XP002048304 abstract & JOURNAL OF THE ELECTROCHEMICAL SOCIETY, AUG. 1997, ELECTROCHEM. SOC, USA, vol. 144, no. 8, pages 2581-2586, ISSN: 0013-4651	1-7, 9-15,18

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 99/ 23074

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
   because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
   because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

        SEE ADDITIONAL SHEET

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest   ☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet (1)) (July 1998)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
WO 9812761	A	26-03-1998	US	5871866 A	16-02-1999
			AU	4410297 A	14-04-1998
			EP	0931361 A	28-07-1999
WO 9740541	A	30-10-1997	EP	0904607 A	31-03-1999
			US	5910382 A	08-06-1999